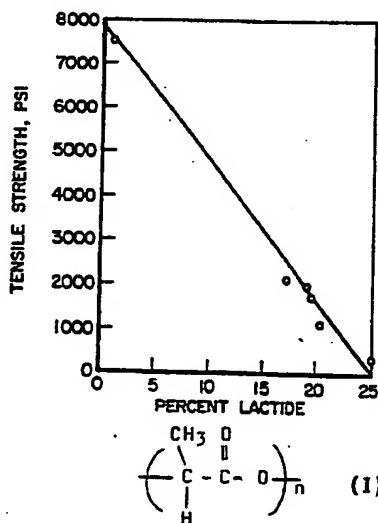




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(54) Title: DEGRADABLE THERMOPLASTIC FROM LACTIDES



## (57) Abstract

Biodegradable compositions of L-lactide, D-lactide, meso D,L-lactide, and racemic D,L-lactide which are suitable for pliable films and other packaging applications are prepared by polymerizing L-lactide, D-lactide, D,L-lactide or mixtures thereof using a catalyst at controlled conditions to allow the polymer in the composition to be plasticized by unreacted lactide monomer. Environmentally biodegradable polymer, composition and process for a polymer and a composition. The biodegradable polymer comprises polymerized lactic acid units of structure (I), where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations where the unoriented polymer has a tensile strength of at least 5,000 psi and tangent modulus of at least 200,000 psi. Another embodiment provides for an environmentally degradable composition comprising blends of a physical mixture of polylactic acid, and a polymer selected from the group consisting of the polymers of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof.

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DEGRADABLE THERMOPLASTIC FROM LACTIDES

The present application is derived from and claims priority of the following eight U.S. applications: The application entitled PLIABLE BIODEGRADABLE PACKAGING THERMOPLASTICS FROM LACTIDES having Serial No. 5 07/229,896, filed August 8, 1988; and the application entitled BIODEGRADABLE REPLACEMENT OF CRYSTAL POLYSTYRENE having Serial No. 07/229,939, filed August 8, 1988; and the application entitled BLENDS OF POLYLACTIC ACID having Serial No. 07/229,894, filed August 8, 1988; and the application entitled DEGRADABLE IMPACT MODIFIED POLYLACTIDES 10 having Serial No. 07/317,391, filed March 1, 1989; and the application PLIABLE BIODEGRADABLE PACKAGING THERMOPLASTICS FROM LACTIDES having attorney docket number PF 2767-1, filed July 31, 1989; and the application entitled BIODEGRADABLE REPLACEMENT OF CRYSTAL POLYSTYRENE having attorney docket number PF 2771-1, filed July 31, 1989; and the 15 application entitled BLENDS OF POLYLACTIC ACID having attorney docket number PF 2772-1, filed July 31, 1989; and the application entitled DEGRADABLE IMPACT MODIFIED POLYLACTIDES having attorney docket number PF 2781-1, filed on July 31, 1989. All of the above applications having Battelle Memorial Institute as assignee.

20 FIELD OF THE INVENTION

In a first embodiment, the present invention relates to plasticized polymers of L-lactide, D-lactide, D,L-lactide and mixtures thereof suitable for packaging applications conventionally served by nondegradable plastics (e.g. polyethylene). The first embodiment 25 further relates to a method for producing pliable films and other packaging items and to the unique product thereof. The invention has utility in producing a product that has the characteristics of the usual plastics yet is biodegradable.

In a second embodiment, the invention discloses a material and 30 process of preparing it which is an offset, that is a replacement for crystal polystyrene, sometimes known as orientable polystyrene or OPS. The material is an offset for the OPS but is composed of a polyester

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capable of biodegrading in the environment over approximately 1 years time. The material is a polyester, comprised of polymerized lactic acid, prepared from either D-lactic acid or L-lactic acid, and D,L-lactic acid. The ratio of the two polymerized monomer units, the process treatment and in some cases certain adjuvants, determine the precise physical properties required for the exacting requirements of an OPS offset. Thus, at approximately a ratio of 90/10, L-lactic/D,L-lactic acid, the polymerized lactic acid (PLA) is a well behaved thermoplastic that is clear, colorless, and very stiff. As such it is very suitable for preparing films, foams, and other thermoformed items of disposable or one-way plastic. Having served its purpose as a packaging plastic, the PLA slowly environmentally biodegrades to innocuous products when left on or in the environment. This harmless disappearance can help alleviate the mounting problems of plastic pollution in the environment.

In a third embodiment, the invention relates to the blending of conventional thermoplastics with polylactic acid. This provides novel, environmentally degradable thermoplastics. The environmentally degradable thermoplastics are useful in a wide variety of applications.

The third embodiment further relates to a method for producing pliable films and other packaging items and to the unique product thereof. The invention has utility in producing a product that has the characteristics of the usual plastics yet is environmentally degradable.

A fourth embodiment of the invention relates to the blending of compatible elastomers with polylactides. This provides impact-resistant modified polylactides that are useful in a wide variety of applications including those where impact-modified polystyrene would be used.

The fourth embodiment further relates to a method for producing packaging items and to the unique product thereof. The invention has utility in making a product that has the characteristics of the usual impact-resistant plastics yet is environmentally degradable.

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BACKGROUND OF THE INVENTION

There is a need for an environmentally biodegradable packaging thermoplastic as an answer to the tremendous amounts of discarded plastic packaging materials. U.S. plastic sales in 1987 were 53.7 billion pounds of which 12.7 billion pounds were listed as plastics in packaging. A significant amount of this plastic is discarded and becomes a plastic pollution that is a blot on the landscape and a threat to marine life. Mortality estimates range as high as 1-2 million seabirds and 100,000 marine mammals per year.

10 A further problem with the disposal of plastic packaging is the concern for dwindling landfill space. It has been estimated that most major cities will have used up available landfills for solid waste disposal by the early 1990's. Plastics comprise approximately 3 percent by weight and 6 percent of the volume of solid waste.

15 One other disadvantage of conventional plastics is that they are ultimately derived from petroleum, which leaves plastics dependent on the uncertainties of foreign crude oil imports. A better feedstock would be one that derives from renewable, domestic resources.

However, there are good reasons for the use of packaging plastics. 20 They provide appealing aesthetic qualities in the form of attractive packages which can be quickly fabricated and filled with specified units of products. The packages maintain cleanliness, storage stability, and desirable qualities such as transparency for inspection of contents. These packages are known for their low cost of production 25 and chemical stability. This stability, however leads to very long life of plastic, so that when its one time use is completed, discarded packages remain on, and in, the environment for incalculably long times.

The polymers and copolymers of lactic acid have been known for 30 some time as unique materials since they are biodegradable, biocompatible and thermoplastic. These polymers are well behaved thermoplastics, 100 percent, truly biodegradable in an animal body via hydrolysis over a time period of several months to a year. In a wet environment they begin to show degradation after several weeks and disappear in 35 about a year's time when left on or in the soil or seawater. The

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degradation products are lactic acid, carbon dioxide and water, all of which are harmless.

In practice, lactic acid is converted to its cyclic dimer, lactide, which becomes the monomer for polymerization. Lactic acid is potentially available from inexpensive feedstocks such as cornstarch or corn syrup, by fermentation, or from petrochemical feedstocks such as ethylene. Lactide monomer is conveniently converted to resin by a catalyzed, melt polymerization, a general process well-known to plastics producers. By performing the polymerization from an intermediate monomer, versatility in the resin composition is permitted. Molecular weight can be easily controlled. Compositions can be varied to introduce specific properties.

Homopolymers and copolymers of various cyclic esters such as glycolide, lactide, and the lactones have been disclosed in numerous patents and scientific publications. Early patents disclosed processes for polymerizing lactic acid, lactide, or both, and did not achieve high molecular weight polymers with good physical properties, and the polymer products were frequently tacky, sticky materials, without good physical properties. See, for example, U.S. Patents 1,995,970; 2,362,511; and 2,683,136. The Lowe patent, U.S. Patent 2,668,162 first teaches the use of pure glycolide and lactide to achieve high molecular weight polymers and copolymers of lactide. Lactide is the dilactone of lactic acid and is an internal ester of lactic acid. When lactide is formed, byproduct water is eliminated, permitting the lactide subsequently to be ring-opened polymerized to linear polyester of high molecular weight without tedious condensation methods. Copolymerization of lactide and glycolide imparted toughness and improved thermoplastic processability as compared to the homopolymers. Polymers and copolymers of excellent physical properties were obtained by using the intermediate, lactide, to form PLA. Copolymers of lactide and glycolide are disclosed by the Lowe patent which are tough, clear, cold-drawable, stretchable, and capable of forming at 210 C into self-supporting films.

Similar disclosures in the patent and other literature developed the processes of polymerization and copolymerization of lactide to

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produce very strong, crystalline, orientable, stiff polymers which were fabricated into fibers and prosthetic devices that were biodegradable and biocompatible, sometimes called absorbable. The polymers slowly disappeared by hydrolysis. See, for example, U.S. Patents 2,703,316; 5 2,758,987; 3,297,033; 3,463,158; 3,531,561; 3,620,218; 3,636,956; 3,736,646; 3,797,499; 3,839,297; 3,982,543; 4,243,775; 4,438,253; 4,496,446; European Patent Application 0146398, International Application WO 86/00533, and Offenlegendsschrift 2,118,127.

Other patents teach the use of these polymers as stiff surgical 10 elements for biomedical fasteners, screws, nails, pins, and bone plates. See, for example, U.S. Patents 3,739,773; 4,060,089; and 4,279,249.

Controlled release devices, using mixtures of bioactive substances with the polymers and copolymers of lactide and/or glycolide, have been 15 disclosed. See, for example, U.S. Patents 3,773,919; 3,887,699; 4,273,920; 4,419,340; 4,471,077; 4,578,384; 4,728,721; R.G. Sinclair, Environmental Science & Technology, 7 (10), 955 (1973). R.G. Sinclair, Proceedings, 5th International Symposium on Controlled Release of Bioactive Materials, 5.12 and 8.2, University of Akron Press, 1978. 20 These applications of lactide polymers and copolymers required tough, or glassy materials, that were grindable and did not disclose physical properties for obvious use in thermoplastic packaging materials.

Some mention has been disclosed in the prior art for use of lactide copolymers for obvious packaging applications. Thus, in the 25 aforementioned patent to Lowe, clear, self-supporting films are noted of a copolymer of lactide and glycolide. In U.S. Patent 2,703,316 lactide polymers are described as film formers, which are tough and orientable. "Wrapping tissue" was disclosed that was tough, flexible, and strong, brittle, or pliable. However, to obtain pliability the 30 polylactide must be wet with volatile solvent, otherwise, stiff and brittle polymers were obtained. The lactide monomer is specified as having a melting point greater than 120 C. L-lactide monomer melts at 95 C and D,L-lactide melts at 128 C. This is an example of the prior art which teaches special modifications of lactide polymers to obtain 35 pliability. Thus, in U.S. Patent 3,021,309, lactides are copolymerized

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with delta valerolactone and caprolactone to modify lactide polymers and obtain tough, white, crystalline solids. Soft, solid copolymer compositions are mentioned only with the copolymer of caprolactone and 2,4-dimethyl-4-methoxymethyl-5-hydroxypentanoic acid lactone, not with  
5 lactide compositions. U.S. Patent 3,284,417 relates to the production of polyesters which are useful as plasticizers and intermediates for the preparation of elastomers and foams. This patent excludes lactides and uses compositions based on 7 to 9 membered ring lactones, such as epsilon caprolactone, to obtain the desired intermediates. No tensile  
10 strength, modulus, or percent elongation data are given. U.S. Patent 3,297,033 teaches the use of glycolide and glycolide-lactide copolymers to prepare opaque materials, orientable into fibers suitable for sutures. It is stated that "plasticizers interfere with crystallinity, but are useful for sponge and films". Obvious in these disclosures is  
15 that the lactide polymers and copolymers are stiff unless plasticized. This is true also of U.S. Patent 3,736,646, where lactide-glycolide copolymers are softened by the use of solvents such as methylene chloride, xylene, or toluene. In U.S. Patent 3,797,499 copolymers of L-lactide and D,L-lactide are cited as possessing greater flexibility  
20 in drawn fibers for absorbable sutures. These fibers have strengths greater than 50,000 psi with elongation percentages of approximately 20 percent. Moduli are about one million psi. These are still quite stiff compositions compared to most flexible packaging compositions, reflecting their use for sutures. U.S. Patent 3,844,987 discloses the  
25 use of graft and blends of biodegradable polymers with naturally occurring biodegradable products, such as cellulosic materials, soya bean powder, rice hulls, and brewer's yeast, for articles of manufacture such as a container to hold a medium to germinate and grow seeds or seedlings. These articles of manufacture are not suitable for  
30 packaging applications.

U.S. Patent 4,620,999 discloses a biodegradable, disposable bag composition comprised of polymers of 3-hydroxybutyrate and 3-hydroxybutyrate/3-hydroxyvalerate copolymer. Lactic acid, by comparison, is 2-hydroxy propionic acid. U.S. Patent 3,982,543 teaches the use of  
35 volatile solvents as plasticizers with lactide copolymers to obtain

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pliability. U.S. Patents 4,045,418 and 4,057,537 rely on copolymerization of caprolactone with lactides, either L-lactide, or D,L-lactide, to obtain pliability. U.S. Patent 4,052,988 teaches the use of poly (p-dioxanone) to obtain improved knot tying and knot security for  
5 absorbable sutures. U.S. Patents 4,387,769 and 4,526,695 disclose the use of lactide and glycolide polymers and copolymers that are deformable, but only at elevated temperatures. European Patent Application 0108933 using a modification of glycolide copolymers with polyethylene glycol to obtain triblock copolymers which are taught as suture  
10 materials. As mentioned previously, there is a strong consensus that pliability is obtained in lactide polymers only by plasticizers which are fugitive, volatile solvents, or other comonomer materials.

Copolymers of L-lactide and D,L-lactide are known from the prior art, but citations note that pliability is not an intrinsic physical  
15 property. U.S. Patent 2,758,987 discloses homopolymers of either L- or D,L-lactide which are described as melt-pressable into clear, strong, orientable films. The properties of the poly-L-lactide are given as: tensile strength, 29,000 psi; percent elongation, 23 percent, tensile modulus 710,000 psi. The poly-D,L-lactide properties were: 26,000 psi  
20 tensile strength; 48 percent elongation; and a tensile modulus of 260,000 psi. Copolymers of L- and D,L-lactide, that is copolymers of L- and D,L-lactic acid, are disclosed only for a 50/50 by weight mixture. Only tack point properties are given (Example 3). It was claimed that one antipodal (optically active, e.g., L-lactide) monomer  
25 species is preferred for the development of high strength. The homopolymers of L-lactide and D,L-lactide, as well as the 75/25, 50/50, and 25/75, weight ratio, of L-/D,L-lactide copolymers are exemplified in U.S. Patent 2,951,828 that discloses the bead polymerization of alpha-hydroxy-carboxylic acids. The copolymers have softening points of 110-  
30 135 C. No other physical property data are given relating to stiffness and flexibility except for physical properties relating to bead size and softening points in the 110 - 135 C range. The 95/5, 92.5/7.5, 90/10, and 85/15, weight ratio, of L-lactide/D,L-lactide copolymers are cited in U.S. Patents 3,636,956 and 3,797,499. They are evaluated as  
35 filaments from drawn fibers and have tensile strengths in excess of

50,000 psi, moduli of about one million, and percent elongations of approximately 20 percent. Plasticizers, the same as in U.S. Patent 3,636,956, above, were used to impart pliability. A snow-white, obviously crystalline polymer, is cited in Offenlegendsschrift 5 2,118,127 for a 90/10, L-lactide/D,L-lactide copolymer. No physical properties were given for this copolymer. The patent teaches the use of surgical elements.

U.S. Patents 3,297,033; 3,463,158; 3,531,561; 3,636,956; 3,736,646; 3,739,773; and 3,797,499 all disclose lactide polymers and 10 copolymers that are strong crystalline, orientable polymers suitable for fibers and suture materials. These disclosures teach the use of highly-crystalline materials, which are oriented by drawing and annealing to obtain tensile strengths and moduli, typically, greater than 50,000 psi and 1,000,000 psi, respectively. Although formability 15 is mentioned into a variety of shaped articles, physical properties of unoriented extrudates and moldings are not mentioned. For example, U.S. Patent 3,636,956 teaches the preparation of a 90/10 weight ratio of L-lactide/D,L-lactide and drawn, oriented fibers are cited. However, it is preferred in this disclosure to use pure L-lactide 20 monomer for greater crystallinity and drawn fiber strength.

U.S. Patent 3,797,499 teaches the copolymerization of 95/5 weight ratio, of L-lactide/D,L-lactide (Example V); however, the material is formed into filaments. In column 5, line 1 Schneider teaches against enhanced properties in the range provided in the present invention. 25 Plasticizers such as glyceryl triacetate, ethyl benzoate and diethyl phthalate are used.

U.S. Patents 3,736,646; 3,773,919; 3,887,699; 4,273,920; 4,471,077; and 4,578,384 teach the use of lactide polymers and copolymers as sustained-drug release matrices that are biodegradable 30 and biocompatible. Again, physical properties of the polymers from ordinary thermoforming methods such as film extrusion or molding are not mentioned.

Of particular interest, U.S. patent 4,719,246 teaches the blending of homopolymers of L-lactide, D-lactide, polymers or mixtures thereof; 35 and copolymers of L-lactide or D-lactide with at least one nonlactide

comonomer. The blending is intended to produce compositions having interacting segments of poly(L-lactide) and poly(D-lactide).

Canadian Patent 808,731 cites the copolymers of L- and D,L-lactide where a divalent metal of Group II is part of the structure. The 5 90/10, L-/D,L-lactide copolymer (Example 2) and the L-lactide homopolymer were described as "suitable for films and fibers". The 90/10 copolymer is described as a snow-white copolymer and the homopolymer of L-lactide can be molded to transparent films. (The more crystalline polymer should be the opaque, or snow-white material, which is the 10 homopolymer.) The patent discloses "the fact that the novel polylactides of the present invention contain the metallic component of the catalyst in the form of a lactate is believed to be of significance". Furthermore, "the polylactides find utility in the manufacture of films and fibers which are prepared by conventional thermoplastic resin manu- 15 facturing methods". No physical property data are given on the strength and flexibility of the films.

Canadian Patent 863,673 discloses compositions of L-lactide and D,L-lactide copolymers in the ratios of 97/3, 95/5, 92.5/7.5, 90/10, and 85/15 ratios of L-/D,L-lactide, respectively. These were all 20 characterized as drawn filaments for surgical applications. Tensile strength, approximately 100,000 psi, was high, elongation was approximately 20 percent and plasticizers were mentioned to achieve pliability. D,L-lactide compositions of less than 15 weight percent are claimed.

25 Canadian Patent 923,245 discloses the copolymers of L- and D,L-lactide (Example 15). The 90/10 copolymer is described as a snow white polylactide. The polylactides prepared by the methods of the patent are stated to have utility in the manufacture of films or fibers prepared by conventional thermoplastic resin fabricating methods.

30 U.S. Patent 4,719,246 teaches the use of simple blending of poly L-and poly (D-lactide), referred to as poly (S-lactide) and poly (R-lactide), polymers of mixtures thereof; and copolymers of L-lactide or D-lactide with at least one nonlactide comonomer. The examples are all physical mixtures. The special properties of the "interlocking" stem 35 from racemic compound formation (cf. "Stereochemistry of Carbon

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Compounds", E. L. Eliel, McGraw-Hill, 1962, p. 45). Racemic compounds consist of interlocked enantiomers, that is, the D and L forms (or R and S) are bonded to each other by polar forces. This can cause a lowering, or raising, of the crystalline melting points, depending on whether the D to D (or L to L) forces are less, or greater, than the D to L forces. Required of polymer racemic compounds to enhance the effect (and stated in U.S. Patent 4,719,246, Column 4, line 48) are homopolymers, or long chain lengths, of both D and L. The great symmetry or regularity of these structures permit them to fit together, or interlock, by very regular polar forces, either because they are the same, or mirror images. This leads to considerable crystallinity. The art of racemic compounds has a long history that goes back to classical chemistry.

U.S. patent 4,661,530, discloses the mixtures of a poly (L-lactic acid) and/or poly (D,L-lactic acid) and segmented polyester urethanes or polyether urethanes. Biodegradable materials are formed that are useful in synthetic replacements of biological tissues and organs in reconstructive surgery.

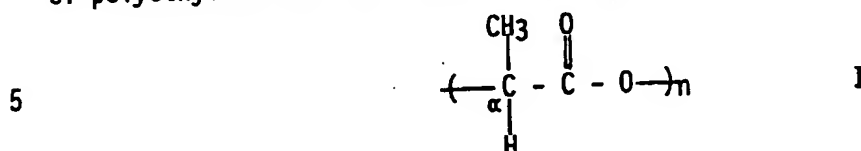
Nowhere in the prior art is it disclosed that lactide polymers, are capable of pliable, highly-extensible compositions by the use of lactide monomers, lactic acid, or oligomers of lactic acid or lactide as the plasticizer. None of the prior compositions are suitable for well-defined packaging needs of the thermoplastic polymers' industry.

It will be appreciated by those skilled in the art that duplicating the properties of one thermoplastic with another is not predictable. Thus, with crystal polystyrene, or OPS, there are exacting requirements for satisfactory performance of the polystyrene, which has been developed over many years to meet manufacturing and end-use specifications of OPS grades.

### 30 BRIEF DESCRIPTION OF THE INVENTION

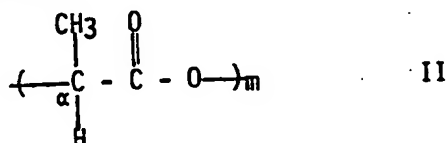
The general teaching of the invention, and first embodiment, is that homopolymers of L-lactide, D-lactide, and D,L-lactide and copolymers of mixtures thereof that have been plasticized with lactide monomer(s), lactic acid or oligomers of lactide or of lactic acid have

utility as well behaved thermoplastics which can mimic properties of the usual environmentally nondegradable plastics, (e.g., the properties of polyethylene and the like). This composition has the formula:



and is intimately plasticized with a plasticizer selected from the group consisting of lactide, lactic acid, oligomers of lactic acid, and mixtures thereof. The oligomers of lactic acid further are preferably represented by the formula II, where m is an integer:  $2 \leq m < 75$ . However, m is preferably  $2 \leq m \leq 10$ . The plasticizer preferably comprises from 2 to 60 weight percent of the polymer. The polymers may be derived from monomers of lactide selected from the group consisting of L-lactide, D-lactide, meso D,L-lactide and mixtures thereof.

15 Preferably n is  $150 \leq n \leq 20,000$ .



Lactide monomer can be present in an amount of from 5 to 40 weight percent of the polymer while lactide oligomer or lactic acid and its oligomers may be present in an amount of from 2 to 60 weight percent. This composition allows many of the desirable characteristics of polyethylene such as pliability, transparency, and toughness.

Further provided is a process for producing the biodegradable composition. The process includes the steps of mixing, heating, and melting one or more lactide monomers and catalyst; polymerizing the monomers of the solution to form a polymer at a temperature sufficiently low to allow the polymerization reaction to be stopped prior to complete polymerization; monitoring the level of monomer; and stopping the reaction prior to complete polymerization at an amount of monomer determined by the monitoring; so that unreacted monomer is trapped in association with the polymer.

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Further provided is a process for producing a plasticized polymer of polylactic acid that comprises mixing, heating, and melting one or

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more lactide monomers and a catalyst; polymerizing the monomers of the solution to form a polymer without stopping the reaction; and incorporating plasticizer into the polymer whereby the plasticizer is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, oligomers of lactic acid, and mixtures thereof.

A second embodiment of the invention includes a process for producing an environmentally biodegradable composition and an environmentally biodegradable composition useful as a replacement for polystyrene comprising polylactic acid units of the formula I where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units, wherein the polymer is prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight, where the unoriented polymer has a tensile strength of at least 5000 psi and tangent modulus of at least 200,000 psi and dispersed plasticizer of 0.1 - 5 weight percent.

A third embodiment of the invention teaches the process for producing an environmentally degradable composition and an environmentally degradable composition comprising blends of a physical mixture of polylactic acid; and one or more polymers selected from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof.

A fourth embodiment teaches the process for producing an environmentally degradable composition and an environmentally degradable composition is disclosed comprising blends of a physical mixture of polylactic acid and blend-compatible elastomers that provide improved impact resistance to the blended composition. Such an elastomer may be, for example, a Hytrel™, a segmented polyester which is a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long chain segments of polyether glycol. One example is known by the trade name as Hytrel™ 4056 (DuPont) segmented polyester.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing the relationship between percent lactide in the composition as plasticizer and tensile strength.

Figure 2 is a graph showing the relationship between percent lactide in the composition as plasticizer and elastic modulus.

Figure 3 is a graph showing the relationship between percent oligomer in the composition as plasticizer and tensile strength where curve A is for a 90/10 copolymer and curve B is for a 92.5/7.5 copolymer.

10 Figure 4 is a graph showing the relationship between percent oligomer in the composition as plasticizer and the elastic modulus where curve A is for a 90/10 copolymer and curve B is for a 92.5/7.5 copolymer.

Figure 5 illustrates the differential scanning calorimetry (DSC) plot of unannealed 90/10, L-/D,L-lactide copolymer of Example 5B.

Figure 6 illustrates the DSC of the material of Example 5B after remaining at 70 C for 100 minutes.

Figure 7 illustrates the DSC of the material of Example 5B after annealing in 185 F overnight.

20 Figure 8 illustrates the DSC of the material of Example 5B that has been blended with 5 percent calcium lactate.

Figure 9 compares the melt viscosity versus shear rate characteristics of polystyrene and the lactide polymer prepared as in Example 8B.

25 Figure 10 illustrates a DSC for the copolymer of Example 8B.

Figure 11 illustrates a DSC for the L-lactide homopolymer that is added to the copolymer of Example 8B.

Figure 12 illustrates a DSC for the blended composition of Example 23 of the copolymer of Example 8B and a homopolymer of L-lactide.

30 Figure 13 illustrates a differential scanning calorimetry (DSC) plot of 90/10, L-/D,L-lactide copolymer blended with 5 weight percent polystyrene.

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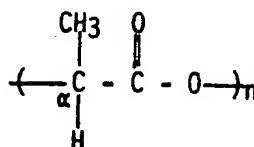
DETAILED DESCRIPTION OF THE INVENTION  
AND PREFERRED EMBODIMENTS

First General Embodiment

The environmentally biodegradable compositions disclosed herein  
5 are completely degradable to environmentally acceptable and compatible  
materials. The intermediate products of the degradation: lactic acid  
and short chain oligomers of lactide or lactic acid are widely  
distributed naturally occurring substances that are easily metabolized  
by a wide variety of organisms. Their natural end degradation products  
10 are carbon dioxide and water. Contemplated equivalents of these  
compositions such as those that contain minor amounts of other  
materials, fillers, or extenders can also be completely environmentally  
degradable by proper choice of materials. The compositions herein  
provide environmentally acceptable materials because their physical  
15 deterioration and degradation is much more rapid and complete than the  
conventional nondegradable plastics that they replace. Further, since  
all or a major portion of the composition will be polylactic acid,  
and/or a lactic acid derived lactide or oligomer, no residue or only a  
small portion of more slowly degrading residue will remain. This  
20 residue will have a higher surface area than the bulk product and an  
expected faster degradation rate.

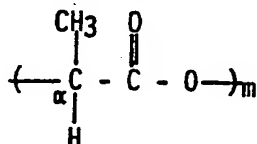
The general application of the invention results in the first and  
general embodiment of the invention. The homopolymers of D-lactide, L-  
lactide, D,L-lactide as well as copolymers of D-lactide, L-lactide; D-  
25 lactide, D,L-lactide; L-lactide, D,L-lactide; and D-lactide, L-lactide,  
and D,L-lactide all produce materials useful in the invention when  
plasticized by lactide monomers, lactic acid, oligomers of lactide,  
oligomers of lactic acid, and mixtures thereof. The plasticizer may be  
produced by stopping the reaction before polymerization is completed.  
30 Optionally additional plasticizer consisting of lactide monomers (D-  
lactide, L-lactide, D,L-lactide, or mixtures thereof), lactic acid,  
oligomers lactide or oligomers of lactic acid, and mixtures thereof can  
be added to the polymer. The polymer is defined by the formula:

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where n is the degree of polymerization (number of repeating units),  
 5 and is plasticized with a plasticizer derived from incomplete polymer-  
 ization of the monomers used to produce the polymer. The more  
 intimately the plasticizer is integrated with the polymer the better  
 are its characteristics. If desired additional monomer or oligomer can  
 be added to any residual monomer or oligomer remaining in the  
 10 composition. The oligomers of lactic acid useful for a plasticizer are  
 defined by the formula II, where m is an integer:  $2 \leq m < 75$ , however,  
 the preferable range is:  $2 \leq m \leq 10$ .



II

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The proportions of L-lactide, D-lactide, and D,L-lactide are not  
 critical to obtaining flexible thermoplastics. The parts of L-lactide,  
 D-lactide, and D,L-lactide can vary over a wide, weight-ratio to form a  
 homopolymer or copolymer. The lactide monomers employed in accordance  
 20 with the invention are available commercially so that neither the  
 monomeric reactant per se nor the method by which it is prepared  
 constitute any portion of the invention.

D-lactide is a dilactone, or cyclic dimer, of D-lactic acid.  
 Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-  
 25 lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide  
 comprises a mixture of D- and L-lactide. When used alone herein, the term  
 "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-  
 lactide.

One of the methods reported in the literature for preparing a  
 30 lactide is to dehydrate lactic acid under high vacuum. The product is  
 distilled at a high temperature and low pressure. Lactides and their  
 preparation are discussed by W. H. Carothers, G. L. Dorough and M. J.  
 Johnson (J. Am. Chem. Soc. 54, 761-762 [1932]); J. Gay-Lussac and J.  
 Pelouse (Ann. 7, 43 [1833]); C. A. Bischoff and P. Walden (Chem. Ber.

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26, 263 [1903]; Ann. 279, 171 [1984]); and Heinrich Byk (Ger. Pat. 267,826 [1912]); through Chem. Abstr. 8, 554, 2034 [1914]).

The optically active acids can be prepared by direct fermentation of almost any nontoxic carbohydrate product, by-product or waste, utilizing numerous strains of the bacterial genus Lactobacillus, e.g. Lactobacillus delbrueckii, L. salivarius, L. casei, etc. The optically active acids can also be obtained by the resolution of the racemic mixture through the zinc ammonium salt, or the salt with alkaloids, such as morphine. L-lactide is a white powder having a molecular weight of 144. If an impure, commercially-available product is employed in accordance with the present invention, it is preferable to purify it by recrystallization from anhydrous methyl isobutyl ketone. The snow-white crystals of L-lactide melt at 96-98 C.

D,L-lactic acid which is used in the preparation of D,L-lactide is available commercially. The D,L-lactic acid can be prepared synthetically by the hydrolysis of lactonitrile (acetaldehyde cyanohydrin) or by direct fermentation of almost any nontoxic carbohydrate product, by-product or waste, utilizing numerous strains of the bacterial genus Lactobacillus. D,L-lactide is a white powder having a molecular weight of 144. If an impure, commercially-available product is employed in accordance with the present invention, I prefer to purify it by recrystallization from anhydrous methyl isobutyl ketone. One such commercially available product comprising a mushy semisolid melting at 90-130 C was recrystallized from methyl isobutyl ketone and decolorized using charcoal. After three such recrystallizations, the product was tumble-dried in vacuo under a nitrogen bleed for 8 to 24 hours at room temperature. The snow white crystals thus obtained comprise a D,L-lactide mixture melting from 115-128 C.

In preparing the compositions in accordance with the invention, it is preferred to carry out the reaction in the liquid phase in a closed, evacuated vessel in the presence of a tin ester of a carboxylic acid containing up to 18 carbon atoms. The compositions however, can also be prepared at atmospheric pressure with the polymerization system blanketed by an inert gas such as, for example, nitrogen. If polymerization is conducted in the presence of oxygen or air, some

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discoloration occurs with a resulting decrease in molecular weight and tensile strength. The process can be carried out at temperatures where the polymerization is sluggish in its later stages so as to trap residual monomer in the viscous polymer melt. Preferred temperatures for this purpose are generally between the melting points of pure L-lactide and pure D,L-lactide, or between 95 to 127 C. While in no way wishing to limit the scope of the invention it is presently believed that below about 129 C, the following occurs:

1. The lactide monomer mixture of L- and D,L-lactide monomers melt to form a eutectic mixture, which melts to a mobile fluid that is an intimate solution of one, two, or three monomers.
2. The fluid melt is polymerized by catalyst to form an increasingly viscous solution and eventually unreacted monomer is trapped in association with the polymer as a solution, rather than as a distinct heterogeneous phase. The monomer no longer can react since the reaction is extremely diffusion controlled and cannot contact the low concentration of active end-groups of the polymer.
3. The polymerization ceases or slows considerably so that at room temperature the blend of monomer and polymer are a solid solution that imparts plasticization, clarity, and flexibility to the composition.
4. The catalyst deactivates so that subsequent melt-fabrication does not reinitiate the polymerization.
5. The plasticized composition is quite stable since the residual monomer is very high boiling, e.g., lactide boiling point is 142 C at 8 torr, and is tightly associated with its open-chain tautomer, polylactide.

Alternatively, the process can be carried out at any temperature between the melting point of the L-lactide and 200 C and lactic acid or lactide is subsequently melt or solvent-blended into the polymer as a further processing step. Temperatures above 200 C are undesirable because of the tendency of the copolymer to be degraded. Increasing the temperature within the range of 95 to 200 C generally increases the speed of the polymerization. Good results are obtained by heating a

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mixture of L-lactide and D,L-lactide at a temperature between about 110 C and 160 C.

The catalysts employed in accordance with the invention are tin esters of carboxylic acids containing up to 18 carbon atoms. Examples of such acids are formic, acetic, propionic, butyric, valeric, caproic, caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic and benzoic acids. Good results have been obtained with stannous acetate and stannous caprylate.

The catalyst is used in normal catalytic amounts. In general, a catalyst concentration in the range of about 0.001 to about 2 percent by weight, based on the total weight of the L-lactide and D,L-lactide is suitable. A catalyst concentration in the range of about 0.01 to about 1.0 percent by weight is preferred. Good results were obtained when the catalyst concentration is in the range of about 0.02 to about 0.5 percent by weight. The exact amount of catalyst in any particular case depends to a large extent upon the catalyst employed and the operating variables including time and temperature. The exact conditions can be easily determined by those skilled in the art.

The reaction time of the polymerization step, per se, is governed by the other reaction variables including the reaction temperature, the particular catalyst, the amount of catalyst and whether a liquid vehicle is employed. The reaction time can vary from a matter of minutes to a period of hours, or days, depending upon the particular set of conditions which are employed. Heating of the mixture of monomers is continued until the desired level of polymerization is detected. The level of polymerization can be determined by analysis for residual monomers. As discussed previously, the reaction temperature can be chosen to enhance the incorporation of monomer and provide plasticized compositions coming directly out of the polymerization reactor. The reaction can be halted at such time that the composition has attained the conversion of monomer to polymer that is desired to achieve the desired plastization. In the preferred embodiment of the invention, approximately 2 to 30 percent lactide is left unreacted, depending on the plasticization to be achieved.

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In general it is preferred to conduct the polymerization in the absence of impurities which contain active hydrogen since the presence of such impurities tends to deactivate the catalyst and/or increase the induction time. It is also preferred to conduct the polymerization  
5 under substantially anhydrous conditions.

The copolymers of the invention can be prepared by bulk polymerization, suspension polymerization or solution polymerization. The polymerization can be carried out in the presence of an inert normally-liquid organic vehicle such as, for example, aromatic hydrocarbons,  
10 e.g., benzene, toluene, xylene, ethylbenzene and the like; oxygenated organic compounds such as anisole, the dimethyl and diethyl esters of ethylene glycol; normally-liquid saturated hydrocarbons including open chain, cyclic and alkyl-substituted cyclic saturated hydrocarbons such as hexane, heptane, cyclohexane, alkylcyclohexanes, decahydronaphthalene and the like.  
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The polymerization process can be conducted in a batch, semi-continuous, or continuous manner. In preparing the lactide monomeric reactants and catalyst for subsequent polymerization, they can be admixed in any order according to known polymerization techniques.  
20 Thus, the catalyst can be added to either of the monomeric reactants. Thereafter, the catalyst-containing monomer can be admixed with the other monomer. In the alternative, the monomeric reactants can be admixed with each other. The catalyst can then be added to the reactant mixture. If desired, the catalyst can be dissolved or  
25 suspended in an inert normally-liquid organic vehicle. If desired, the monomeric reactants either as a solution or a suspension in an inert organic vehicle can be added to the catalyst, catalyst solution or catalyst suspension. Still further, the catalyst and the monomeric reactants can be added to a reaction vessel simultaneously. The  
30 reaction vessel can be equipped with a conventional heat exchanger and/or a mixing device. The reaction vessel can be any equipment normally employed in the art of making polymers. One suitable vessel, for example, is a stainless steel vessel.

The environmentally biodegradable compositions produced in  
35 accordance with the present invention depending upon the L-lactide, D-

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lactide, meso D,L-lactide ratios, find utility in articles of manufacture, such as films, fibers, molding and laminates, which are prepared by conventional fabricating methods. These articles of manufacture are contemplated for nonmedical uses i.e. outside the body where they can substitute for the common environmentally nondegradable plastics.

Filaments, for example, are formed by melt-extruding the copolymer through a spinneret. Films are formed by casting solutions of the biodegradable compositions and then removing the solvent, by pressing solid biodegradable compositions in a hydraulic press having heated platens, or by extrusion through a die.

Various techniques including slow cooling and rapid cooling can be employed in preparing moldings from the copolymers of the invention.

Contemplated equivalents of the compositions of the invention are those that contain minor amounts of other materials. The copolymers produced in accordance with the present invention can be modified, if desired, by the addition of a cross-linking agent, other plasticizers, a coloring agent, a filler and the like.

Cross-linking can be effected by compounding the compositions with free-radical initiators such as cumene hydroperoxide and then molding at elevated temperatures. This can improve heat-and solvent-resistance. Curing can also be effected by compounding the copolymers with multifunctional compounds such as polyhydric alcohols and molding, or thermoforming under heat and vacuum. Graft-extruder reactions to effect curing of the polyesters is an obvious method of cross-linking and chain-extending the copolymers.

In preparing moldings, a filler can be incorporated in the compositions prior to curing. A filler has the function of modifying the properties of a molding, including hardness, strength, temperature resistance, etc. Known filler materials include aluminum powder, powdered calcium carbonate, silica, kaolinite (clay), magnesium silicate and the like. Of particular advantage is starch, which blends well with the compositions to obtain a blend which is totally environmentally biodegradable. Other property modifications can be

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effected by melt blending the compositions with other polymers and copolymers of the lactides, glycolides, and caprolactone.

The compositions prepared according to the present invention can be used in producing reinforced laminates according to known  
5 procedures. In general, laminates are made from a fibrous mat or by assembling a multiplicity of sheets of material to form a matrix which is consolidated into a unitary structure by flowing molten precursor or composition through the fibrous material and curing it while in a mold or hydraulic press to form the polymer. Fibers which are used in  
10 forming the matrix include natural and synthetic fibers such as cellulose derived from wood, cotton, linen, hemp, and the like, glass, nylon, cellulose acetate and the like.

The compositions of the invention and their preparation are further illustrated by the following specific examples.

15 Example 1

80/20, L-lactide/racemic D,L-lactide

160 grams of L-lactide and 40 grams of racemic D,L-lactide, both of high purity (Purac, Inc., triply recrystallized), were charged into a 500 ml, round-bottom flask and purged with dry nitrogen overnight.  
20 10 ml of stannous octoate is dissolved in 60 ml of anhydrous toluene, and 10 ml of the solvent is distilled to a Dean-Stark trap to effect dryness of this catalyst solution by azeotropic distillation. From the 10 ml of stannous octoate in 50 ml of dry toluene a 0.20 ml portion is removed with a syringe and injected into the lactides in the reaction  
25 flask. The nitrogen purge is continuous via a syringe needle connection that enters the reaction flask through a rubber septum and vents via a piece of tubing that connects to a bubbler. The nitrogen flow is maintained at 1-3 bubbles per second. The flask was heated in an oil bath maintained at 123-127 C. During the first part of the heating the  
30 lactides melt and are mixed thoroughly by swirling. Thereafter, the products become quite viscous. After 20 hours of heating, the flask and the colorless, transparent products are removed from the heating bath, cooled, the flask broken, and shocked with liquid nitrogen to remove glass from the product. The copolymer was molded in a heated

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hydraulic press. Compression molding to 5 to 10 mil thick films was possible at 20,000 lb pressure, at 170 C, in a time period of 2 minutes. The films were evaluated for their tensile properties on a Instron tester, and the results are listed in Table 1. Samples 1/8 inch thick were also molded for impact strength testing. A thermal gravimetric analysis (TGA) of the product was performed, noting the weight loss upon heating the sample to 150 C in 4 minutes and holding the temperature at 150 C for 60 minutes. The weight loss of the sample was 19.5 percent and nearly complete in 60 minutes. The weight loss is attributed to loss of lactide monomer. Results of differential scanning calorimetry (DSC) reveal that the composition has an endotherm beginning about 110 C, becoming more pronounced as the temperature increases to 200 C. No melting point was observed. Specimens were annealed at 185 F overnight and reexamined. They remained transparent, colorless and pliable. Samples of the copolymer could be remolded 6 times without any discoloration or obvious loss of strength. Thin films were clear, transparent, colorless, and quite flexible, despite the repeated molding.

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TABLE 1. PROPERTIES OF COPOLYMERS<sup>(a)</sup> OF L-LACTIDE AND D,L-LACTIDE WHEN PLASTICIZED BY LACTIDE

Example No.	1	2	3
5 Film thickness, mil	8	8	10
Tensile strength, 1000 psi, ASTM D638	3.9	1.7	7.9
Elongation, percent	28	806	3.5
10 100 percent modulus, 1000 psi	0.74	--	--
200 percent modulus, 1000 psi	1.20	--	--
Tangent modulus, 1000 psi	36.6	--	289
Izod impact strength, ft-lb/in. <sup>(b)</sup>	0.63	--	0.4
M <sub>w</sub> , 1000's	540	281	341
15 M <sub>n</sub> , 1000's	270	118	97.5
Residual lactide, <sup>(c)</sup> percent	19.5	27.8	2.7

(a) 80/20, weight ratio, of L-/racemic D,L-lactide.

(b) 1/8 inch, notched samples.

20 (c) By isothermal TGA weight loss at 150 C.

Example 2

In a 3-liter, round-bottom flask was charged 1.84 Kg of L-lactide, 0.46 Kg of racemic D,L-lactide and 2.3 ml of the stannous octoate solution, similar to Example 1. The mixture was purged with argon for 25 3 hours, then heated isothermally in a 125 C oil bath. The mixture melts, was mixed thoroughly by swirling, and forms a homogeneous, transparent, colorless fluid whose viscosity increases substantially after several hours. After 64 hours the flask was removed from the heating bath, cooled, and the glass removed from the clear, 30 transparent, solid product. The rubbery composition was guillotined

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into slices and ground to 1/8 inch, or smaller, size in a grinder with dry ice. The grind was dried in an air circulating oven at 100 F for several hours, then vacuum dried overnight at ambient temperature. Compression-molded films were prepared as described in Example 1 and the films were examined for their tensile properties and weight loss by TGA as shown in Table 1.

### Example 3

In a 250-ml, round bottom flask was placed 79.98 g of L-lactide, 20.04 g of racemic D,L-lactide, and 0.20 ml of stannous octoate solution, similar to Example 1. The flask was swept by nitrogen through inlets and outlets and heated in a 125 C oil bath. The mixture melted to a colorless and fluid liquid that was thoroughly mixed by swirling the flask. After 2 hours, the oil bath temperature was increased to 147 C, and after 14 hours total heating time, the temperature was decreased to 131 C. Total heating time was 18 hours. The product is transparent, colorless, and glassy. It was evaluated, similar to the preceding examples and the results are recorded in Table 1.

Examples 1 to 3 reveal the effect of reaction temperature on the properties of the copolymers as occasioned by the resulting composition.

### Example 4

Films of the copolymers of Examples 1 and 3 were immersed in water for several months. After 3 weeks, the copolymer of Example 1 became hazy while that of Example 3 remained clear for approximately 2 months; after 3 months the film of Example 3 became noticeably hazy and the film of Example 1 is white and opaque. The water that had been in contact with the film of Example 1 tastes acidic while that of Example 3 is tasteless.

Inspection of the data of Table 1 reveals that the copolymer of Example 1 is an environmentally biodegradable replacement for polyethylene. Those skilled in the art will recognize that the physical properties of the copolymer are an excellent combination

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useful for many packaging applications. Its tensile strength and initial tangent modulus compare favorably with polyethylene compositions used, for example, in plastic trash bags, general film wrap, plastic shopping bags, sandwich wrap, six pack yokes and the like. The shape of the stress-strain curves are approximately the same for both the copolymer and that for a linear low density polyethylene composition commonly used in trash bag compositions. A comparison of properties are shown in Table 2.

TABLE 2. COMPARISON OF POLYETHYLENE TO POLYLACTIC ACID POLYMERS

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Property	LDPE-(a) NA 272	LLDPE(b)	Lactide Copolymer(c)
15 Tensile strength, 1000 psi, ASTM Standard C	2.18	2.9	3.90
Elongation, %	261	500	280
Tangent modulus, 1000 psi	54.9	51.0	36.6
20 100% modulus, 1000 psi	1.77	--	0.74
200% modulus	1.82	--	1.20
HDT, (d) 264 psi, F	95	99	122

- 25 (a) Linear low density polyethylene, 5-10 mil, 2-in./min.,  
our experiments.  
(b) Linear low density polyethylene, data from computer file.  
(c) Copolymer of L-lactide/racemic D,L-lactide, Example 1.  
(d) Heat deflection temperature.

30 The lactide polymerization can be stopped at incomplete monomer-to-polymer conversion in a controllable fashion. This is illustrated in Examples 1 and 2. The lactide monomer binds very intimately with polymers of lactides. Alternatively, the compositions can be derived

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by mixing of lactide with preformed polymer. In that case, the lactide added can be the same or different with respect to stereochemistry, i.e., L-, D-, or D,L-lactide to that used to make the polymer.

The compounding can be accomplished by blending the molten polymer with lactide monomer in conventional processing equipment such as a mill roll or a twin screw compounder. The normally stiff, glassy, lactide polymers are flexibilized by the lactide and remain transparent, colorless, and very nearly odorless. The lactide is not very fugitive, requiring heating, and a nitrogen sweep, typically, 170-200 C for 20-60 minutes to remove the lactide in a gravimetric analysis. Neither is the lactide visible in films under an optical microscope. The lactide domains are submicron in size. This flexibilizing of the polylactic acid suggests its use as an environmentally biodegradable replacement for polyolefin, disposable, packaging films.

#### Examples 5-16

A series of experiments were performed in which copolymers of L- and racemic D,L-lactide were prepared, melt blended with variable amounts of lactide, and the physical properties of the blends evaluated as a function of the lactide composition. Monomer lactide content was assayed by a previously developed isothermal, thermogravimetric analysis (TGA). The lactide contents were measured before and after compounding and molding into films.

It was observed that open roll, 2 roll, milling tended to volatilize the lactide at temperatures required for the very high, molecular weight lactide copolymers. These losses could be minimized by masterbatching or by using lower molecular weight lactide copolymers (and their lower attendant mixing temperatures). A better mixing and blending method was a conventional, twin screw extruder, which minimized volatile losses. Some results are shown in Table 3. The blends of polylactide and lactide plasticizer are quite pliable, becoming increasingly so with increasing lactide content. They are colorless and transparent. Only a very faint (pleasant) odor of lactide is detectable and no discernable taste of lactide was

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noticeable. The Table 3 plasticized film samples were tear resistant, easily foldable, and can be punctured without shattering or tearing. They stiffen somewhat when placed in a cooler (5 C, 40 F), but remain flexible and creasible without breaking. These films noticeably soften  
5 in the hand, indicating a glass transition temperature below 37 C. When the lactide content is less than 20 percent, the films will have a rattle typical of a polyolefin film. At greater lactide contents the films have the drape and "warm" feel of a PVC.

As shown in Table 3, the elastic moduli (initial tangent moduli)  
10 can be relatively high, similar to a linear low density polyethylene (LLDPE). This is an indication of potential form stability. Lower moduli and tensile strengths are similar to low density polyethylene (LDPE). Physical properties, as a function of lactide content, were plotted as shown in Figures 1 and 2. Referring to Table 3, at  
15 approximately 17-20 percent lactide content, the tensile properties are similar to polyethylenes used in trash bags and shopping bags.

At lower lactide contents, the blends have a similarity to polypropylene. Some data can be compared in Table 3. Table 4 defines the conventional plastics used in the comparisons.

TABLE 3. TENSILE PROPERTY COMPARISONS OF PLASTICIZED PLA(a)

Example No.	Composition	Lactide, %TGA	Elastic Modulus, 1000 psi	1% Secant Modulus, 1000 psi	Yield Strength, 1000 psi	Strain at Yield, %	Break Strength, 1000 psi	Strain at Break, %
5	90/10, L-/D, L-Lactide Copolymer	1.3	289	291	0	0	7.5	3
10	"	17.3	119	119	2.23	4	2.29	288
6	"	19.2	95.5	90.3	1.97	5	4.24	536
7	"	19.6	88.7	88.7	1.72	4	2.12	288
8	"	20.5	50.3	50.3	1.21	5	2.16	338
9	"	25.5	33.7	22.9	0.32	4	2.44	546
15	"							

(a) ASTM 882; all samples were compression molded 5-10 mil films except Examples 13 and 14; strain rate 1.0 in/in min for all, D,L-lactide is racemic.

(CONTINUED) TABLE 3. TENSILE PROPERTY COMPARISONS OF PLASTICIZED PLA(a)

5	Example No.	Composition	Lactide, %TGA	Elastic Modulus, 1000 psi	1% Secant Modulus, 1000 psi	Yield Strength, 1000 psi	Strain at Yield, %	Break Strength, 1000 psi	Strain at Break, %
10	11	LDPE (b)	--	41.3	40.6	1.51	17	1.60	365
	12	LLDPE (c)	--	44.4	42.7	1.66	16	1.66	599
	13	Bi axially (d) oriented PE	--	38.9	41.1	1.69	16	4.78	838
	14	" (e)	--	35.6	38.5	1.68	16	5.20	940
	15	HDPE (f)	--	127.8	120.9	3.48	9	1.95	216
	16	pp (g)	--	174	174	5.08	5	7.34	6
	15								

(b) USI low density polyethylene (petrothene No. 213).  
 (c) Exxon linear low density polyethylene (LLPE 6202,57).  
 (d) Machine direction.  
 (e) Cross machine direction.  
 (f) Phillips high density polyethylene (HMN 5060).  
 (g) Chisso polypropylene (XF 1932, melt index 0.52).

20

TABLE 4. MANUFACTURERS' DATA

5	Supplier	Trade Name and/or Grade	Density, gm/cu cm	Recommended Melt Temperature, F	Tensile Strength at Yield	Elastic Modulus in Flexure, 35 psi	Melt Index gm/10 min
	LDPE (USI)	Petrothene No. 213	0.924	360-550	1820	0.37	8.0
10	LLDPE (Exxon)	6202.57	0.926	425	1700	0.53	12.0
	HDPE (Phillips)	HMN 5060	0.950	425-525	3600	1.75	6.0
	80% LLDPE (Exxon) 20% HDPE (Processing oil)	LPX 86 (Octene base)	0.927	260	--	--	0.8
15	Polypropylene (PP-Chisso)	XF1932	0.91	450-500	5872	3.05	0.52
	Polystyrene (Amoco)	RI	1.05	400	7900	4.50	1.8

Table 3 reveals some data for lactide and polylactide mixtures. The results do not differ remarkably from similar compositions of Examples 1 and 2, prepared by other means. However, those skilled in the art will recognize that the precise physical properties will vary somewhat depending on the intimacy of the mixture, the tensile testing conditions, and the fabrication technique for preparing the films. Comparisons from Table 3 reveal that the lactide-polymer mixtures have a broad range of controllable compositions that mimic many conventional, nondegradable plastic types.

10 Example 17

An oligomeric polylactic acid (OPLA) was prepared for mixing with polylactides as follows. An 88 percent solution of L-lactic acid (956 g) was charged to a 3-neck flask (1 liter) fitted with a mechanical stirrer and a pot thermometer. The reaction mixture was concentrated under a nitrogen purge at 150-190 C at 200 mm Hg for 1 hour until the theoretical water of dilution was removed. No catalyst was used except for lactic acid and its oligomers. This temperature and vacuum were maintained and distillation continued for 2 hours until 73 percent of the theoretical water of dehydration was removed.

20 The total time required was 3 hours. At this time the reaction was stopped. The water samples and the pot oligomer were titrated with 0.5N NaOH. Some lactic acid, 26.2 g, was found in the water distillate. The pot oligomer (OPLA) was also refluxed with excess 0.5N NaOH, then back titrated with standard H<sub>2</sub>SO<sub>4</sub>. The data are recorded in Table 5. The OPLA flows well when hot, and shows some cold flow. It has a degree of polymerization of 3.4. It was used in Example 20 where it was melt blended with the polymer of Example 19.

TABLE 5. CHARACTERIZATION OF OPLA OF EXAMPLE 1

5	Percent Dehydrated, Theoretical	Titratable Acid, percent	Titratable Ester, percent	Total Expressed as Lactic Acid percent	Degree of Polymerization
	58	34.4	82.4	116.8	3.4

#### 10 Example 18

The procedure of Example 17 was repeated except the distillation was conducted more slowly. After 8 hours of heating during which the temperature was slowly advanced from 63 to 175 C at 200 mm Hg, a sample of the pot was titrated to reveal 62.2 percent of theoretical water  
15 removal. Titration revealed a degree of polymerization of 4.3. The molecular weight of the OPLA was further advanced over 2 hours by heating at 179 C and using a vacuum pump. The OPLA was no longer soluble in 0.1N NaOH, was water white, and would cold flow. This material is a second example of an OPLA preparation with somewhat  
20 higher degree of polymerization as compared to Example 1. It was mixed with polylactide in Examples 22 and 25. It is estimated that the degree of polymerization was about 6-10.

#### Example 19

A polymer of lactide was prepared by methods similar to Example 3.  
25 A 90/10, weight percent L-/racemic D,L-lactide copolymer was melt polymerized using 0.02 parts per hundred, anhydrous stannous octoate catalyst. In a similar manner a 100 percent L-lactide homopolymer (L-PLA) was prepared. The copolymer was melt blended with the homopolymer at 350 F in a twin-screw extruder at a weight ratio of 90/10,  
30 copolymer/homopolymer. Gel permeation chromatography (GPC) of the blend reveals a weight-average molecular weight ( $M_w$ ) of 182,000 and a

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number-average molecular weight ( $M_n$ ) of 83,000. Residual lactide monomer by thermogravimetric analysis (TGA) was 1.7 weight percent. This blend was mixed with the oligomeric polylactic acid of (OPLA) of Example 17 to provide Example 20. The tensile properties are listed in Table 6.

#### Example 20

The polymer of Example 19 was melt blended with the OPLA of Example 17 on an open, 2-roll, mill for 20 minutes at 325 F. The mix was compression molded into films and tested as shown in Table 6. The GPC molecular weights were smooth, monomodal distributions ( $M_w/M_n = 2.6$ ) with  $M_w = 192,000$  and  $M_n = 73,000$ .

TABLE 6. PROPERTIES OF MELT BLENDS OF 90/10 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt. % Polymer Oligomer	Lactide, % TGA	Elastic Modulus, 1000 psi (a)	Break Strength, psi (a)	Strain at Break, % (a)	Tg, °C (b)
5						
19	100 <sup>(c)</sup>	0	298	7500	3	55
20	91 <sup>(c)</sup>	9 <sup>(d)</sup>	275	6113	2	--
10	21	100 <sup>(e)</sup>	0	308	7478	58
22	70 <sup>(e)</sup>	30 <sup>(f)</sup>	254	5052	3	42
23	60 <sup>(e)</sup>	40 <sup>(f)</sup>	202	3311	2	38
24	50 <sup>(e)</sup>	50 <sup>(f)</sup>	106	2334	25	35
15	25	40 <sup>(e)</sup>	60 <sup>(f)</sup>	36	1180	35

(a) ASTM 882; 5-10 mil, compression-molded films; strain rate 1.0 in./in./min.

(b) Glass transition temperature by differential scanning calorimetry.

(c) A blend of 90% of a 90/10, L-/D, L-lactide\*copolymer with 10% poly(L-lactide), Example 19.

(d) Oligomeric PLA of Example 17.

(e) A blend of 80% of a 90/10, L-/D, L-lactide\*copolymer with 20% poly(L-lactide).

(f) Oligomeric PLA of Example 18.

\* racemic

Example 21-25

- The copolymer of Example 19 was melt blended with 20 percent of the L-PLA described in Example 19. The blend is listed as Example 21 in Table 6, where its analyses and tensile properties are listed.
- 5 Example 21 was, in turn, melt blended with various amounts of the OPLA of Example 18 and these were tested as before and listed in Table 6, Examples 22 to 25. Table 7 lists the GPC molecular weights of these compositions. The tensile strengths and moduli are compared to the weight percentages of OPLA in Figures 3 and 4 (Lower Curves).

TABLE 7. MOLECULAR WEIGHTS AND GLASS TRANSITION TEMPERATURES OF 90/10 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt % Copolymer      Oligomer	Res. (a) Mon., %	GPC x 10 <sup>-3</sup> (b)			M <sub>w</sub> /M <sub>n</sub>	T <sub>g</sub> , (c) °C
			M <sub>n</sub>	M <sub>w</sub>	M <sub>z</sub>		
5	21    100 <sup>(d)</sup>	0	76	175	410	2.3	58
	22    70 <sup>(e)</sup>	30 <sup>(f)</sup>	67 <sup>(g)</sup>	136	299	2.0	42
	23    60 <sup>(e)</sup>	40 <sup>(f)</sup>	61 <sup>(g)</sup>	112	211	1.8	38
	24    50 <sup>(e)</sup>	50 <sup>(f)</sup>	62 <sup>(g)</sup>	114	223	1.8	35
	25    40 <sup>(e)</sup>	60 <sup>(f)</sup>	69 <sup>(g)</sup>	120	207	1.7	35

(a) Residual monomer by TGA.

(b) Molecular weight by GPC.

(c) Glass transition temperature by DSC.

(d) A blend of 90% of 90/10, L-/D,L-lactide copolymer with 10% L-Pla.

(e) Example 21.

(f) Example 18.

(g) After blending; melt-blending on an open mill roll at 325 F.

All D,L-lactide is racemic.

Examples 26-30

A second series of copolymers was blended with the OPLA. A 92.5/7.5, L-/D, L-lactide copolymer was prepared by methods similar to Examples 19 and 21. This is Example 26 of Tables 8 and 9. It was melt  
5 blended with the OPLA of Example 18 on an open, 2-roll mill at 325 F for approximately 20 minutes. The blends were compression molded into 3-5 mil thick films and their tensile properties and GPC molecular weights measured. The properties are recorded in Tables 8 and 9, and plotted in Figures 3 and 4. The second series of blends revealed  
10 significantly higher values for the tensile properties although the molecular weights were lower. This may be due to lower residual lactide monomer and/or the change in high polymer composition. All of the OPLA polylactide blends could be easily molded into tack free, transparent films.

TABLE 8. PROPERTIES OF MELT BLENDS OF 92.5/7.5 POLYLACTIDES AND OLIGOMERIC POLYLACTIC ACID

Example Number	Composition, wt. % Polymer (c) Oligomer (d)	Lactide, % TGA	Elastic Modulus, 1000 psi, (a)	Break Strength, psi (a)	Strain at Break, % (a)	Tg <sup>(b)</sup> °C
26	100	0	338	10,527	4	61
27	80	20	346	9,144	4	52
28	70	30	346	5,675	2	46
29	60	40	249	5,617	3	36
30	50	50	112	1,984	119	36

15 (a) ASTM 882; 3-5 mil compression-molded films; strain rate 1.0 in./in./min.

(b) Glass transition temperature by differential scanning calorimetry.

(c) 92.5/7.5, L-/D,L-lactide copolymer.

(d) Example 18.

20 All D,L-lactide is racemic.

TABLE 9. MOLECULAR WEIGHTS OF 9.25/7.5,  
L-/RACEMIC D,L-LACTIDE COPOLYMERS

5	Example No.	% OPLA	GPC x 10 <sup>-3(a)</sup>		
			M <sub>n</sub>	M <sub>w</sub>	M <sub>z</sub> M <sub>w</sub> /M <sub>n</sub>
10	26	0	63	124	228 1.95
	27	20	60	108	189 1.81
	28	30	48	80	125 1.66
	29	40	59	96	151 1.65
	30	50	56	92	141 1.64

(a) GPC

Examples 31 and 32

- 15 Film specimens with, and without plasticizer were exposed to seawater at Daytona, Florida from March through May. The pH of the water varied from 7.3 to 7.6 and the salinity from 33.2 to 38.4 ppt. The water gradually warmed in the test from 15 to 27 C. The specimens were cut into strips and tensile tested before, and after, periodic
- 20 intervals in the seawater. The results are shown in Table 10. All of the samples showed whitening and physical degradation, which became progressive with time. Without plasticizer the samples showed whitening and degradation after six weeks in the seawater. The OPLA polylactide blend degraded faster, revealing clear evidence of
- 25 degradation after 3 weeks. The incorporation of 20 percent lactide provoked immediate whitening and obvious degradation after one week of exposure.

TABLE 10. PHYSICAL PROPERTIES AFTER SEAWATER EXPOSURE

5	Example Number	Composition	Tensile Properties, 1000 psi <sup>(a)</sup>						Strain, % Break
			Seawater Exposure Weeks	Elastic Modulus	1% Secant Modulus	Yield Strength	Break Strength	Yield	
10	31	90/10 copolymer 5% L-PLA	0	305	292	--	7.6	--	4.7
			3(b)	315	301	--	7.1	--	3.1
			6(c)	317	317	--	7.3	--	3.0
			9(d)	228	230	--	6.2	--	3.0
			12(e)	355	343	--	3.9	--	1.0
15	20	90/10 copolymer with 10% oligomer	0	275	275	--	6.1	--	2.0
			3(b)	291	281	--	6.8	--	2.9
			6(e)	246	246	--	3.9	--	2.0
			9(d)	211	105	2.2	1.4	3	2.0
			12(e)	103	103	--	1.7	--	1.0
20	32	90/10 copolymer with 1% fumaric acid	0	300	298	--	7.0	--	3.0
			3(b)	292	291	--	6.5	--	2.5
			6(c)	318	318	--	6.9	--	2.0
			9(d)	226	223	--	6.1	--	3.0
			12(e)	70	122	--	0.8	--	1.1
25	9	92.5/7.5 co- polymer with 20% lactide	1(e)	--	--	Too brittle to test			

(a) 0.5 x 5 in. strips of film, 12-17 mil; strain rate 1 in./in./min.

(b) 15-21 C, saline seawater, regularly exchanged.

(c) 20-22 C, saline seawater, regularly exchanged.

(d) 22-23 C, saline seawater, regularly exchanged.

(e) 22-27 C, saline seawater, regularly exchanged.

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The above examples establish that an all lactic acid composition can be a pliable thermoplastic useful for flexible, plastic containers. By way of comparison, nonplasticized homopoly (L-lactide) is a highly crystalline polymer with a tensile strength of about 7000 psi with an elongation of 1 percent and an initial modulus of 500,000 psi. It is very brittle, opaque, and crazes easily. It is not a well behaved thermoplastic, nor is it transparent. Poly (racemic D,L-lactide) is an amorphous, glassy, polymer with a glass transition temperature of approximately 50 C, a tensile strength of about 6300 psi, an elongation of approximately 12 percent, and an initial modulus of 160,000 psi. It is also very brittle although transparent. In stark contrast, a polymer of L-lactide/racemic D,L-lactide copolymer that is plasticized with lactide monomer is remarkably different. For example, the plasticized polymers can have a tensile strength of approximately 3900 psi, an elongation of 431 percent, and an initial modulus of 56,000 psi. The plasticized polymer is clear and colorless and the blend must be heated to above 100 C to remove the plasticizer.

Although theory would predict a more amorphous structure as a result of plasticization, what is surprising is the pliable, transparent, stable compositions that can arise, and, secondly, the nearly exact fit of properties needed for certain packaging applications, such as polyethylene. This invention comes at a time when there is a need for such initial properties in a material that is slowly environmentally biodegradable since it could alleviate plastic pollution problems.

It will be apparent to those skilled in the art that extremely intimate blends of high polymers and plasticizers are a rarity. Plasticization allows a wide latitude in the initial physical properties and the time for environmental biodegradation.

The amount of plasticizer in the polymer depends on the compositional characteristics desired. If lactide is used as plasticizer the range is preferably 5 to 40 weight percent whereas if only oligomers of lactide or lactic acid are used the range may be from 2 to 60 weight percent. Surprisingly, oligomer may be added at up to 30 weight

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percent without substantially affecting the tensile strength or modulus. See Figures 3 and 4. Addition of 30 to 60 weight percent oligomers produces significant plasticization and attenuation of physical properties. This adds great economy to the composition since  
5 oligomeric lactic acid is cheaper than high polymer lactic acid. Oligomer may be prepared from lactic acid or any lactide. It is important to note that the oligomer of lactic acid normally contains significant amounts of lactic acid unless removed. This is an important consideration in tailoring compositions having specific  
10 properties. Those skilled in the art and knowing the teachings of this invention will be able to select reaction conditions to obtain appropriate chain lengths for the polymer, and the proportions of polymer and plasticizer so as to obtain fabricated compositions having physical properties similar to commonly used packaging thermoplastics  
15 and yet degrade comparatively rapidly. For example, higher amounts of plasticizer result in polymers having increased flexibility and increasingly tough physical properties, however, an increasing degradation rate will also be obtained. Further, shorter chain lengths for the polymer will require less plasticizer to obtain the same  
20 properties as with longer lengths.

Further provided by the first embodiment of the invention is a process for producing an environmentally biodegradable composition that is a plasticized polymer of polylactic acid having the formula (I). The process comprises preparing one or more lactide monomers and  
25 catalyst; polymerizing the monomers to form a polymer at a temperature sufficiently low to allow the polymerization reaction to be stopped prior to complete polymerization; monitoring the level of monomer to determine the amount of remaining monomer; and stopping the reaction prior to complete polymerization at a determined amount of monomer so  
30 that unreacted monomer of a predetermined amount is trapped in association with the polymer. The lactide monomers of the process are selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. Optionally one may incorporate additional plasticizer into the polymer whereby the  
35 plasticizer is further selected from the group consisting of L-lactide,

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D-lactide, racemic D,L-lactide, meso D,L-lactide, lactic acid, oligomers of lactic acid, oligomers of lactide, and mixtures thereof. Preferably polymerization of the monomers is at a temperature less than 129 C. Further processing of the plasticized polymer into a final  
5 product is preferably at a temperature sufficiently low to retain the plasticizer in the polymer. This temperature may be above 129 C. If additional monomer and/or oligomer are added the retention of monomer is of course not as critical.

Further provided by the first embodiment of the invention is a  
10 process for producing a polymer of formula I comprising preparing one or more lactide monomers and catalyst; polymerizing the monomers to form a polymer; and incorporating plasticizer in a separate step into the polymer whereby the plasticizer is selected from the group consisting of D-lactide, L-lactide, D,L-lactide, oligomers of lactic  
15 acid, and mixtures thereof.

The compositions of the invention should have a tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent and a tangent modulus of 20,000 to 250,000 psi. Preferably for a polyolefin replacement the compositions have a tensile strength of at  
20 least 3000 psi, an elongation to failure of at least 250 percent, and a tangent modulus of at least 50,000 psi.

The homopolymers and copolymers of the present invention are insoluble in water but upon constant contact with water are slowly degradable. However, degradation is fast when compared to polyolefin  
25 compositions that are replaced by the invention. Thus, throwaway objects made from the polymers are environmentally attractive in that they slowly degrade to harmless substances. If objects made from polymers of the invention are incinerated, they burn with a clean, blue flame.

Yet further provided by the first embodiment of the invention is a  
30 method for replacing a thermoplastic composition with the biodegradable composition of the invention where the thermoplastic composition comprises first orientable polymer units, by replacing the first polymer units with a second orientable polymer having an  
35 unoriented tensile strength of 300 to 20,000 psi, an elongation to

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failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi; wherein the second polymer comprises polylactic acid units of the structure in formula I, wherein n is the number of repeating units and n is an integer,  $150 \leq n \leq 20,000$  and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide and mixtures thereof. The method is useful for polyolefin compositions and particularly polyethylene and polypropylene as well as polyvinyl chlorides and polyethylene terephthalate. In addition to the above list the method is useful for replacement of polymers of styrene, vinyl acetate, alkyl methacrylate, alkyl acrylate. It is understood that copolymers made from mixtures of the monomers in the listed group and physical mixtures of the polymers and copolymers of the above group are likewise replaceable.

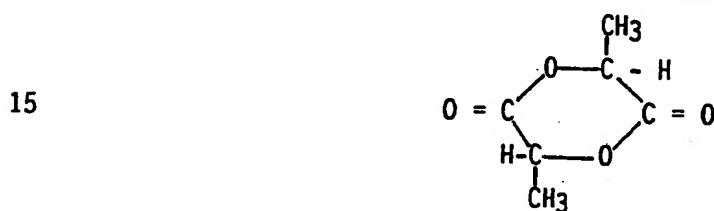
15 Second General Embodiment

The environmentally biodegradable compositions disclosed as a second embodiment herein are completely degradable to environmentally acceptable and compatible materials. The intermediate products of the degradation: lactic acid is a widely distributed naturally occurring substance that is easily metabolized by a wide variety of organisms. Its natural end degradation products are carbon dioxide and water. Contemplated equivalents of these compositions such as those that contain minor amounts of other materials, fillers, or extenders can also be completely environmentally degradable by proper choice of materials. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid and complete than the conventional nondegradable plastics that they replace. Further, since all or a major portion of the composition will be polylactic acid, and/or a lactic acid derived lactide or oligomer, no residue or only a small portion of more slowly degrading residue will remain. This residue will have a higher surface area than the bulk product and an expected faster degradation rate.

The preferred composition of the present invention comprises polymerized lactic acid units with the repeating unit of formula I, wherein n is an integer with a value between 75 and 10,000 and the alpha carbon

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is a random mixture of D and L (or R and S) with a preponderance of one of the pure enantiomeres. When n is low, the polylactic acid, PLA, is easily processible, but is considerably weaker than when n is larger. When n is quite large, e.g., 7000 or greater, the PLA is quite strong but difficult to injection mold. Preferably n is approximately 500 to 3000 for the best balance of melt-processibility and end-use physical properties. The monomers are selected in L (or D)/D,L-ratios of polymerized lactic acid or their cyclic dimer, lactide, as further discussed below. Both lactic acid and lactide achieve the repeating PLA unit, shown above, but lactide is preferred since it more easily obtains the higher molecular weights necessary for good physical properties. Since lactide, which has the structure:



has two alpha carbons which are assymetric, there are three types of lactide, viz., D,D- (or D-); L, L- (or L-); and meso D,L-lactide.

20 D-lactide is a dilactide, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide

25 or racemic D,L lactide. The term dispersed as used herein means the material is homogeneously and intimately mixed with the polymer.

Pure L-PLA has poor processing characteristics, easily crazes and becomes opaque. Pure D,L-PLA processes easily but is not sufficiently rigid to be an adequate OPS offset. The copolymer ratio of between

30 85/15 to 95/5, and preferably 90/10, L-lactide/D,L-lactide is a preferred embodiment of the invention. At higher ratios than 95/5, the copolymer is difficult to thermoform without crazing and easily becomes opaque at room temperature. At lower ratios than 85/15, the lactide copolymers exhibit lower than desirable moduli for OPS offsets. In

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between these limits the copolymers are quenched from the melt in typical manufacturing/processing equipment of plastics technology to achieve films and moldings which are clear, colorless, and extremely rigid. Their properties as formed, above, are closely matched to those  
5 properties of an OPS.

Another advantage of this invention is that the all-lactic acid copolymer can utilize inexpensive feedstocks. Corn syrup via starch and corn can be fermented to either L- or racemic D,L-lactic acid, depending on the microorganism. Racemic D,L-lactic acid is cheaply  
10 obtainable via ethylene which can be oxidized to acetaldehyde, which is reacted with hydrogen cyanide to form lactonitrile, which is hydrolyzed to racemic D,L-lactic acid. Lactide is simply obtained by distillation of lactic acid. No change of the stereochemistry of the asymmetric carbon occurs in transforming lactic acid to lactide by ordinary  
15 distillation/condensation methods.

While the reaction of L-lactide and D,L-lactide is discussed herein, it is to be understood that the reactions specifying L-lactide may also use D-lactide. Thus the reaction of D-lactide and D,L-lactide according to the method described herein will give an equivalent  
20 product; the only difference being that it rotates light in a different direction.

The copolymers of the present invention are preferably formed by heating the mixture of monomers to form a homogeneous melt and adding a catalyst to cause the lactides to undergo a ring-opening polymeriza-  
25 tion. The polymerization is preferably carried out in an inert, anhydrous, atmosphere, such as nitrogen or argon, or in a vacuum. Suitable catalysts include divalent metal oxides and organo-metallic compounds such as stannous octoate, zinc acetate, cadmium acetate, aluminum acetate or butanoate, tin chloride, tin benzoate, and antimony  
30 oxide. Stannous octanote is the preferred catalyst because of its high solubility in the monomers, ease of preparation in anhydrous form, and low toxicity. The amount of catalyst required can vary from approximately 0.02 to 2 percent by weight, based on monomers and is preferably about 0.2 percent. The molecular weight and melt vis-  
35 cosities of the copolymers are controllable by the amount of catalyst

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and/or chain-transfer agents such as glycolic acid. The reaction temperature of the polymerization is between approximately 100 to 200 C. The least color formation occurs below 140 C and the rate of polymerization is best above 135 C. Since racemic D,L-lactide melts at  
5 127 C it is best for conversion of monomer to polymer to polymerize at a temperature above 127 C.

Where clarity and transparency is required, as with OPS offsets, the copolymers of this invention are polymerized in an inert atmosphere above their melting points, which are generally in the 125 to 150 C  
10 range. The molten lactide copolymer can be extruded from the polymerizer in strands and rods, quenched, pelletized and stored in bags for use in subsequent molding and extrusion operations.

Similarly, clarity of thermoformed packaging films and shaped articles is achieved by molding and extruding above the copolymer's  
15 melting points and fast cooling the fabricated item. Thereafter, the copolymers remain transparent unless heated for several hours above their glass transition temperature,  $T_g$ , and below the melting point,  $T_m$ . Slow cooling of thermoformed sheets, slabs, films, and molded items can induce spherulite crystallinity in the copolymers which gains  
20 improvement in the heat stability of the fabricated item, but causes some loss of transparency. Nucleating agents such as sodium benzoate, calcium lactate, and the like, can also induce rapid and substantial crystallinity. A modest amount of drawing of the copolymer, between its  $T_g$  and  $T_m$ , induces orientation of the polymer molecules and can  
25 substantially improve physical properties without loss of transparency.

Blending of different types of lactide polymer or copolymer can substantially change the physical properties. As an example, the melt-blending of the high-melting L-lactide polymer with a lower melting lactide copolymer can provide a transparent material which has a  
30 sufficient amount and type of crystallinity to remain transparent. Those skilled in the art will recognize that transparency in molded films, great stiffness, elevated heat distortion temperature, thermoprocessability, and environmental biodegradability are a rare combination of properties. Thus, the polymers can be blended, as well  
35 as nucleated, oriented, and controlled by molecular weight to provide a

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great deal of latitude in the processibility and final properties in the final compounded thermoplastic.

The copolymers of the present invention will hydrolyze back to lactic acid in the presence of moisture. In the presence of ambient  
5 air and humidity the hydrolysis becomes evident in about 12 to 18 months time. The copolymers then become sticky, somewhat opaque, and very brittle. When immersed in water the copolymers show obvious hydrolysis effects in 1 to 4 months time, depending on the composition, molecular weights, the ambient temperature, their surface-to-volume  
10 ratio, and the particular, aqueous environment the copolymers are placed in. Microorganisms can further reduce the lactic acid to carbon dioxide and water. As an approximate measure, the copolymers have a shelf life of several months, but disappear within about a year when thoroughly wet.

15 The following examples are merely illustrative of the present invention. In Examples 1B to 7B, a composition series was prepared and evaluated. It was discovered, in contrast to the prior art, that there are distinct differences in the processing behavior and physical properties of the L-lactide/D,L-lactide copolymers.

#### 20 Example 1B

In a dry, 500 ml, round-bottom flask was charged 160 g of L-lactide (Purac, Inc., "triple-star" grade) and 40 g of racemic D,L-lactide (Purac, Inc., "triple star" grade). This mixture was heated for approximately 1 hour at 123-129 C under a stopper with a continuous  
25 nitrogen purge through a stopper inlet and outlet. The monomers form a clear melt, which is mixed thoroughly by swirling the melt. Catalyst solution was prepared and dried by azeotropic distillation, that is, 10 ml of stannous octoate (Polysciences, Inc.) was dissolved in 60 ml of toluene; 10 ml of toluene, with trace water, was distilled to a Dean-  
30 Stark trap that was vented via a drying tube. A 0.20 ml quantity of the stannous octoate solution was pipetted into the melt and mixed thoroughly. The nitrogen sweep continues and the melt becomes increasingly viscous over the next 3 hours. Heating continues at 123-127 C for 20-24 hours. The mixture was allowed to cool to room

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temperature and the flask cooled further with liquid nitrogen behind a shield. The glass shatters and is removed from the polymer by tapping. The copolymer is clear and colorless and is evaluated in a series of tests shown in Table 1B. Films were compression molded at 170 C in a  
5 heated hydraulic press for later tensile testing. Slabs, 1/8 inch thick were molded for impact testing by notched Izod, ASTM, D256 and heat deflection temperature, ASTM, D648. Glass transition temperature (T<sub>g</sub>) and melting point (T<sub>m</sub>, center of the endotherm) were evaluated by differential scanning calorimetry (DSC).

10 Examples 2B-7B

The procedures of Example 1B were repeated except that the ratio of L- and racemic D,L-lactide were changed as shown in Table 1B with the test results. The pure L-lactide polymer, Example 7B, would not  
15 always mold well at 170 - 200 C since it frequently crazed badly on cooling in the mold. Frequently, on cooling, it opacified.

TABLE 1B. PROPERTIES OF L-LACTIDE/RACEMIC D,L-LACTIDE COPOLYMERS

Composition, Weight Ratio, L-Lactide/D,L-Lactide (Racemic)		80/20	1B	2B	85/15	87.5/12.5	90/10	4B	5B	6B	7B	white, opaque
Example No.		Color/Transparency colorless & transparent →										
5	Film Thickness, mil	10	5	15	11	5	10	5	10	5	5	
10	Tensile Strength, 1000 psi, ASTM D882	7.9	6.9	8.3	8.6	8.2	9.2	(a)				
-	Elongation, %	3.5	5.8	6.0	7.1	7.2	5.1	(a)				
	Tangent modulus, 1000 psi	289	221	694	210	268	748	--				
15	Izod impact strength(b), ft-lb/in.	--	0.44	0.34	0.31	--	0.41	(a)				
	M <sub>w</sub> , 1000's	--	928	--	--	--	--	--				
	M <sub>n</sub> , 1000's	--	218	--	--	--	--	--				
	T <sub>g</sub> , C(c)	53	53	48	44	--	46	--				
20	T <sub>m</sub> , C(c)	--	--	125	133	--	152	190				

(a) Crazes on cooling, too brittle to test.

(b) Notched samples, impacted on notched side on 1/8 in. thick specimens.

(c) Differential scanning calorimetry in nitrogen with 10 C/min. heating rate.

Example 8B

Similar to Examples 4B and 5B, a 90/10 weight ratio copolymer of L-lactide/racemic D,L-lactide was prepared. Into a dry, nitrogen-swept, 2-liter flask was placed 1045.8 g L-lactide and 116.4 g of racemic D,L-lactide. A 1.0 ml quantity of anhydrous stannous octoate (0.2 ml per ml of toluene) solution was added. The flask was swept with nitrogen overnight, then heated in a 141 C oil bath until the monomers are melted and well mixed, and the heating decreased slowly to 125 C and continued for 72 hours. The polymer slowly whitens on cooling. After removing the glass, the cloudy, colorless, glassy copolymer was evaluated. Gel permeation chromatography obtains a weight-average molecular weight ( $M_w$ ) of 522,000, and a number-average molecular weight ( $M_n$ ) of 149,000.

A DSC of the lactide polymer reveals a strong  $T_m$  at 145 C, see Figure 10. The lactide polymer was melted, quenched, and examined again by DSC to reveal no crystallization or melting points. However, a  $T_g$  appears at approximately 50-55 C. The results show the polymer can be crystalline or amorphous, depending on its heat history.

Examples 9B - 12B

The composition series was extended, using the procedures of Example 1B except other L- and racemic D,L-lactide ratios were used and heating was 2 hours 125 C, 14 hours 125-147 C, then 2 hours 147-131 C. The results are shown in Table 2B.

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TABLE 2B. TENSILE AND MODULUS PROPERTIES OF L-LACTIDE AND D,L-LACTIDE COPOLYMERS

5	Composition, weight Ratio, L-Lactide/ D,L-Lactide (Racemic)	70/30	60/40	20/80	0/100
	Example No.	9B	10B	11B	12B
10	Color/transparency	Colorless/ clear			
	Film thickness, mil	6-9	4-6	4-5	5-7
15	Tensile strength, (a) 1000 psi, ASTM D638(a)	6.9	6.7	5.8	5.6
	Elongation, %	3.2	3.0	2.7	2.8
	Tangent modulus, 1000 psi	287	293	275	278

20 (a) Films were pulled at a jaw separation of 0.2"/min. and chart speed of 5"/min.

The results of the above examples reveal that only certain compositions have the required properties for an OPS offset. The main requirements for an OPS-like material are clarity and colorlessness, tensile strength greater than 7000 psi, tangent modulus (a measure of stiffness) greater than 400,000 psi and well-behaved thermoplasticity. Table 3B lists some side-by-side comparisons of a crystal polystyrene (OPS) and a 87.5 weight percent L-lactide and 12.5 weight percent racemic D,L-lactide random copolymer.

TABLE 3B. PHYSICAL PROPERTY COMPARISONS

10	Property	Poly(lactic acid), Example 3B	Crystal Polystyrene
15	Impact strength, notched Izod, ft-lb/in.	0.4	0.4
	Ultimate tensile strength, psi	8300	7400
	Elongation, %	6.0	4.0
	Elastic modulus, psi	694,000	450,000
20	Deflection temperature, F under load, 264 psi	(a)	200
	Specific gravity	1.25	1.05
	Rockwell hardness	(b)	M75
	Vicat softening point, F	(c)	225
25	Melt flow rate, D1238(G)	40-46(d)	1.7 g/10 min.(e) 1.6 g/10 min.(f)

(a) Depends on heat history.

(b) Shore D = 97.

30 (c) DSC,  $T_m = 125$  C (257 F) at 10 degree/min.

(d) Flow rate decreases at lower temperature.

(e) Listed by manufacturer.

(f) By our experiment.

Example 13B

The copolymer of Example 2B was molded and remolded several times to determine if color would develop in the films and the molecular weights remained high. This determines if the copolymer can be recycled, an important consideration for manufacturing practices. The results of Table 4B show that the copolymer remained completely transparent and colorless after repeated heating and molding despite the fact that the copolymer was repeatedly exposed to air at elevated temperatures.

10                      TABLE 4B. EFFECT OF MOLDING ON LACTIDE COPOLYMER

Example No.	History	Appearance	M <sub>w</sub> , 1000's	M <sub>n</sub> , 1000's	M <sub>w</sub> /M <sub>n</sub>
15	Example 2B(a)	Not molded, directly from polymerization	928	218	--
	Example 13B(a)	Ex. 2B after molding(b)	301	135	2.22
20	Example 13B(a)	Ex. 2B after molding 6 times(b)	137	56.7	2.42

- (a) 85/15, L-lactide/racemic D,L-lactide copolymer.  
 25 (b) Compression molding at 167 C (333 F) for 7 minutes to 5-mil film.

Examples 14B-18B

The copolymers of Examples 2B, 3B and 6B were compression molded into films of approximately 20 to 30-mil thickness and were placed in a heated Instron tester where the films were drawn 5 times their length at 83 C at a rate of 0.5 inch per minute. The films were cooled quickly upon removal from the Instron, and found to be approximately 5-mil in thickness. They were clear and colorless. Tensile properties were evaluated and are listed in Table 5B. When drawn 8 to 10 times

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their length, the films show evidence of crystallinity formation by virtue of haze development and some loss of transparency.

The results demonstrate that very thin films can be made with adequate stiffness and transparency for an OPS offset. Thus, despite the higher density of the lactide copolymers compared to polystyrene, less material can be used for stiff OPS offsets.

TABLE 5B. PROPERTIES OF L-LACTIDE/RACEMIC D,L-LACTIDE COPOLYMERS AFTER ORIENTATION(a)

10	Composition, weight Ratio, L-Lactide/D, L-Lactide (Racemic)	85/15	85/15	85/15	87.5/12.5	95/5
15	Example Number	14B	15B	16B	17B	18B
	Film thickness, mil	5.5	5.0	6.5	5.0	4.0
	Tensile strength, 1000 psi	14.0	14.7	15.0	13.0	16.0
	Elongation, %	31.5	15.4	30.0	23.8	37.4
20	Tangent modulus, 1000 psi	--	564	419	432	513

(a) 5X oriented at 83 C using a draw down speed of 0.5 in./min. on Instron.

#### 25 Example 19B

Films of the copolymers of lactide of Table 1B were immersed in water for several months interval. The copolymers remained clear for approximately 2 months; after 3 months a slight haziness developed. Upon setting on the shelf in humid air and with frequent handling, the films remain virtually unchanged for approximately 1 year although Instron data will show a slow decrease in the strength and elongation after several months. In a landfill, the buried films disappear in 6 months to 2 years, depending on the moisture, pH, temperature,

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composition, surface-to-volume ratio, and biological activity of the landfill. All of the films burn with a clean, blue flame.

#### Example 20B

The lactide copolymer of Example 5B (quenched, compression-molded film) was examined by DSC and found to have less than 2 percent crystallinity, see Figure 5, in the vicinity of 130 C. A 1/8 inch thick sample of the copolymer of Example 5B was annealed in a 185 F oven for 16 hours. The sample turned hazy and the DSC of the sample, see Figure 7 revealed a pronounced increase in the crystallinity. The sample showed a 264 psi heat deflection temperature (HDT) of 90 to 95 C. A similar sample without annealing exhibited a heat deflection temperature of 50 to 55 C, which corresponds to its T<sub>g</sub>.

#### Example 21B

Calcium lactate, 5 weight percent, was blended on a heated mill roll with the lactide copolymer of Example 5B at 170 C for approximately 5 minutes. The blend was stripped off the roll as a sheet and examined. It was stiff, strong, and hazy. Optical microscopy at 82X reveals heterogeneous domains in the size range of from a few microns to 30 microns. DSC reveals a substantial increase in crystallinity in the vicinity of 145 C, see Figure 8, which remain on quenching and reheating. The results, above, comparing Examples 8B, 20B, and 21B, show that nucleating agents are more prompt and efficient in inducing crystallinity in lactide copolymers. Nucleating agents such as salts of carboxylic acids may be used, salts of lactic acid are preferred.

#### Example 22B

In a 500-ml, 3-neck, round bottom flask, equipped with a mechanical stirrer and a nitrogen inlet and outlet, was placed 180.7 g of L-lactide and 40.2 g of racemic D,L-lactide (both Boehringer and Ingelheim, grade S). The contents of the flask were heated to 110 C under a nitrogen sweep to melt the lactides and 20.1 g of polystyrene (Amoco R3, melt index 3.5 g/10 min.) was added. The polystyrene

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swelled highly and partially dissolved with stirring overnight while advancing the heat to 185 C. The temperature was decreased to 141 C and 0.2 ml of anhydrous stannous octoate solution (0.2 ml/ml of toluene) was added. The stirrer was turned off and the lactides  
5 allowed to polymerize at 141 C over 3 days time. The highly swollen, polystyrene floats to the top after turning off the stirrer. The lower, polylactide phase was cooled and examined by DSC. The sample has a low Tg, approximately 35 C, and is otherwise lacking in apparent temperature transitions. Compression-molded films are clear,  
10 colorless, and very pliable. These results indicate that the polystyrene thoroughly interrupts crystallinity formation.

#### Example 23B

The lactide copolymer of Example 8B was mill-roll blended with 20 weight percent of the homopolymer of L-lactide produced in Example 7B.  
15 A sample of the homopolymer was analyzed by DSC, see Figure 11. The blended sample was examined by DSC and found to have a Tg of 59-63 C and strong Tm's at 150 and 166 C, see Figure 12. Films were clear to slightly hazy, depending on their cooling rate after pressing. Quenched samples easily crystallize on heating to approximately 80 - 90  
20 C. As a result the heat deflection temperature of the blend is now quite high. The blend becomes hazy at 80-90 C but does not deflect with heat as does the unblended 90/10 copolymer. Tensile data as shown in Table 6B were obtained on unoriented, compression-molded films and compared to similarly obtained data for polystyrene.

TABLE 6B. COMPARISON OF BLEND OF POLYLACTIDE OF EXAMPLE 23B WITH CRYSTAL POLYSTYRENE

	Example 23B <sup>(a)</sup>	Crystal Polystyrene <sup>(a,b)</sup>
5		
Film thickness, mil	8	14
Tensile strength, ASTM D882, 1000's psi	7.7	6.0
Elongation, %, to yield	6.5	3.2
10 Tangent modulus, 1000,'s psi	323	267

(a) Thin films, unoriented, compression-molded specimens

(b) Melt Index 1.7

15 This example illustrates that melt blending is an excellent way to improve the properties of the copolymer so that advantageous properties similar to polystyrene are realized. The higher the amount of homopolymer based on L-lactide (or D-lactide) blended with the polymer the higher will be the heat deflection temperature, however, haziness  
 20 will also increase. Thus addition of homopolymer may be combined with other methods of increasing polystyrene like properties while still retaining clarity

As a further example orienting films produced from the polymer increases the tensile properties. At eight to ten times the draw the  
 25 physical properties are still increasing but the material becomes hazy. The degree of orientation will thus need to be controlled and combined with the other property changing methods to achieve optimum polystyrene like characteristics.

#### Examples 24B-27B

30 Examples 24B to 27B were polymerizations of lactide with controlled amounts of chain transfer agents, demonstrating that molecular weights can be controlled using transfer agents such as glycolic acid. The results are shown in Table 7B. A nearly straight

line relationship exists between the amount of transfer agent and the reciprocal of the weight average molecular weight. A preferred chain transfer agent is lactic acid.

TABLE 7B. MOLECULAR WEIGHT CONTROL USING CHAIN TRANSFER AGENTS

5

Example No.	PPH of(a) CTA	$M_n$ (b)	$M_w$ (b)	$M_w/M_n$
24B	0.22	13,500	107,300	8.0
10 25B	0.45	12,800	66,700	5.2
26B	0.90	7,300	29,900	4.1
27B	1.80	4,700	13,900	2.9

15 (a) Parts of glycolic acid chain transfer agent (CTA) per hundred parts of lactide in polymerization recipe.

(b) Gel permeation chromatography in tetrahydrofuran solvent, 23 C, with 10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup>, and 10<sup>3</sup> anstrom columns, number average,  $M_n$ , and weight average,  $M_w$ , molecular weights are calculated compared to monodisperse polystyrene standards.

#### 20 Example 28B

A 4.0 mil, compression-molded film of the lactide copolymer of Example 2B was evaluated as a barrier film by ASTM methods. The results are shown in Table 8B. The lactide copolymer is a much better barrier to carbon dioxide and oxygen than is polystyrene. By  
25 comparison to some other polymer barrier films, the lactide copolymer is an adequate barrier film for many packaging applications.

TABLE 8B. EXAMPLE 28B PERMEABILITY TO GASES<sup>(a)</sup>

5	Units	Lactide Copolymer, Example 2B	Crystal <sup>(b)</sup> Polystyrene	Terephthalate	Vinylidene <sup>(b)</sup> Chloride- vinyl Chloride Copolymer
10	cc/100 sq. in./ 24 hr/atmos				
	CO <sub>2</sub>	32.1	900	15-25	3.8-44
	O <sub>2</sub>	19.9	350	6-8	0.8-6.9

- 15 (a) ASTM D1434-75, Example 2B was a 4.0 mil, compression-molded film.  
 (b) Values from Modern Plastics Encyclopedia.

Example 29B

20 Sheets, 1/8 inch thick of the lactide copolymers of Examples 18-6B were immersed overnight in a mixture of petroleum ether and methylene chloride. At ratios of 70/30 to 60/40, petroleum ether/methylene chloride, the copolymers would foam when placed in boiling water. Irregular, but well expanded, foams would form.

Example 30B

25 A comparison was made of the melt viscosities of a commercial, crystal polystyrene (Type 201, Huntsman Chemical Corp.) and the lactide polymer of Example 8B. The melt index, ASTM D1238 (G), of the polystyrene was 1.6 g/10 min. at 200 C using the standard 5 Kg weight. The melt index of the lactide polymer was 40-46 g/10 min. under the same conditions, however, at 160 C the value was 8.0 g/10 min. A more detailed comparison of melt viscosities was obtained by observing the  
 30 melt viscosities of the two polymers in an Instron Capillary Viscometer. The comparative results are shown in Figure 9. The shear rates normally encountered during extrusion and injection molding are approximately 100 to 1000 reciprocal seconds. Inspection of the data

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of Figure 9 shows that the melt viscosity of the lactide polymer at 160 C is very similar to that of the polystyrene at 200 C.

The above results illustrate that lactide polymers can be melt-processed, at lower temperatures than polystyrene, by very similar methods.

#### Examples 31B-34B

Small, test polymerizations of purified (recrystallized and dried) mesolactide (meso D,L-lactide) were carried out as the homopolymer and the copolymer. The molecular weights were evaluated by GPC and compared to analogues of D,L-lactide. The results are presented in Table 9B. The polymers were melt pressed into films and their physical properties evaluated and compared as shown in Table 10B. Within experimental differences of sheet thickness and molecular weight, the copolymers are similar within experimental error. The homopolymer of mesolactide is somewhat weaker.

TABLE 9B. GPC MOLECULAR WEIGHT COMPARISONS OF MESO-AND RACEMIC LACTIDE POLYMERS AND COPOLYMERS

Example Nos.	Composition	Res. Mon., %	GPC x 10 <sup>-3</sup>			
			M <sub>n</sub>	M <sub>w</sub>	M <sub>z</sub>	M <sub>w</sub> /M <sub>n</sub>
31B	D,L-PLA	--	97.5	341	757	3.49
32B	Meso PLA	2.76	62.5	152	264	2.42
33B	90/10, L-/meso	1.67	29	142	301	1.67
34B	90/10, L-/D,L	--	91.3	201	350	2.20

TABLE 10B. PHYSICAL PROPERTY COMPARISON OF D,L- AND MESO-LACTIDE POLYMERS AND COPOLYMERS(a)

Example No.	Polymer Composition	Elastic Modulus, 100 psi	Tensile at Yield Strength, 100 psi	Elongation to Yield %	Film Thickness, mil	Strain Rate in./min.
31B	Homopolymer of D,L-lactide	278	5.6	2.8	5-7	0.25
32B	Homopolymer of meso-lactide	345	3.8	3.5	9	0.25
33B	90/10, L-/meso lactide copolymer	190	7.9	3.8	12-15	0.25
34B	90/10, L-/D,L-lactide copolymer	323	8.6	4.6	4-6	0.25

(a) Compression-Molded films

An overall description of the composition of the second embodiment of the invention includes an environmentally biodegradable polymer comprising polymerized lactic acid units of the structure of formula I, where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units, wherein the polymer is suitable for replacement of polystyrene. The D- and L-units of the polymer may preferably be prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight.

10 An environmentally biodegradable composition with improved properties more like those of polystyrene comprises blends of a physical mixture of polymerized lactic acid units of the structure of formula I, where n is an integer between 75 and 10,000 and the alpha carbon is a random mixture of L- and D-configurations with a preponderance of either D- or L-units, a lactide homopolymer of D-lactide or L-lactide. Compositions having n equal to an integer between 150 and 10,000 have a good balance between strength and melt processability.

A general description of the process for producing the composition of the second embodiment comprises mixing with a catalyst, heating, and melting L-lactide or D-lactide monomer and D,L-lactide monomer whereby the L-lactide monomer or D-lactide monomer is in an amount of 85 to 95 parts by weight and D,L-lactide monomer is in an amount of 15 to 5 parts by weight, to form an intimate solution; polymerizing the solution; and treating the polymer to modify its properties so as to make the polymer suitable as a replacement for polystyrene. The properties of the composition may be adjusted by adding a nucleating agent; adding a D-lactide or L-lactide homopolymer by blending to produce a physical mixture; orienting the polymer; adding a nucleating agent and a D-lactide or L-lactide polymer by blending; adding a nucleating agent and a D-lactide or L-lactide polymer by blending and orienting the polymer; adding chain transfer agents to the polymerization step so as to adjust the characteristics to a polystyrene replacement, annealing at an elevated temperature, and adding

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additional plasticizer where the plasticizer is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof. If a monomer is selected as a plasticizer a unique composition may be obtained by adding monomer that is stereochemically different from that used to obtain the polylactide in the composition. Similarly, addition of oligomer stereochemically different from that which may be obtained during polymerization of the polymer gives a unique product. Color bodies can be excluded by performing the polymerization in an inert atmosphere and at reaction temperatures preferably at 140 C or below. Various combinations of the above treatments can be employed to obtain the optimum characteristics as those skilled in the art will appreciate, once knowing the teachings of the invention.

As can be noted in the aforementioned first embodiment, a higher amount of monomer or oligomer can have significant effect. In the present second embodiment lower amounts of monomer and oligomer are preferred to impart stiffness. Plasticizer present in an amount of 0.1 to 5 percent is preferred. The composition usually contains plasticizer in an amount that depends on polymerization conditions or on the amount added after polymerization. The additional monomer used as plasticizer may be selected from the group: D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof. Oligomers of lactide or lactic acid may also be added. Unique compositions may be obtained by addition of monomer or oligomer stereochemically different from those selected for the polymers in the composition.

Further provided by the second embodiment of the invention is a method for replacing a thermoplastic composition with the biodegradable composition of the invention where the thermoplastic composition comprises first orientable polystyrene units, by replacing the first polymer units with a second orientable polymer having an unoriented tensile strength of at least 5,000 and a tangent modulus of at least 200,000; wherein the second polymer comprises polylactic acid units of the structure in formula I, wherein  $n$  is the number of repeating units and  $n$  is an integer,  $75 \leq n \leq 10,000$ , and the alpha carbon is a mixture of L- and D- configurations with a preponderance of

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either D- or L- units, wherein the polymer is prepared from L- or D-lactide at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide  
5 and mixtures thereof between 0.1 and 5.0 weight percent.

Contemplated equivalents of the compositions of the invention are those that contain minor amounts of other materials. The compositions produced in accordance with the present invention can be modified, if desired, by the addition of a cross-linking agent, other plasticizers,  
10 a coloring agent, a filler and the like.

The compositions herein can be processed by melt fabrication into useful articles of manufacture having a self supporting structure such as disposable containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, packaging films  
15 and the like. The compositions are useful in that they can have the characteristics of the usual polystyrenes and therefore substitute for them yet degrade in the environment. The compositions are especially useful for articles having only a one time use or a short life span in use before disposal.

### 20 Third General Embodiment

A third embodiment discloses the blending of polylactic acid (PLA) with polystyrene (PS), polyethylene (PE), polyethylene terephthalate (PET), and polypropylene (PP). The embodiment discloses that polylactic acid is melt compatible with these conventional  
25 thermoplastics and the effect on their physical properties.

The environmentally degradable compositions disclosed herein are at least partially degradable. That is the polylactic acid portion of the composition will decompose relatively rapidly compared to the more stable portions of the blend and cause a physical deterioration of the  
30 blended material. For example, when the compositions are intimate and homogeneous blends with small domain sizes the physical deterioration will destroy the original formed product. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid than conventional

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nondegradable plastics. Further, since a significant portion of the composition can be polylactic acid, and/or a lactic acid derived lactide or oligomer only a small portion of more slowly degrading thermoplastic residue will remain (e.g. polystyrene). This residue  
5 will have a high surface area and is expected to decompose faster than a bulk formed product.

D-lactide is a dilactone, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide  
10 comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-lactide. Polylactic acid may be prepared from one or more of the above.

#### Example 1C

15 Polystyrene was solvent blended with polylactic acid and solvent cast from  $\text{CH}_2\text{Cl}_2$  to determine optimum compatibility. The solvent cast films were translucent and apparently "noncheesy". A sample, appears homogeneous to the naked eye and resists folding and handling without shredding apart. Optical microscopy at 310X reveals heterogeneous  
20 domains of 3 microns and less. The blend is apparently very compatible. It exhibits no change over 2 years with regard to "blooming" of fugitive material nor does its physical properties show evidence of degradation.

#### Example 2C

25 Polypropylene 8525, Hercules, was similarly melt blended in the Brabender with polylactic acid at 400 F. Ratios of PP/PLA prepared were 100/0 for the control, 90/10, and 75/25.

#### Examples 3C-5C

Melt blends were prepared of polylactic acid with polystyrene.  
30 Both a high molecular weight polystyrene (Piccolastic, E-125, Hercules) and a low molecular weight polystyrene (Piccolastic, D-100) were investigated. Also used was a general purpose polystyrene, (Huntsman

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polystyrene 208), a crystal polystyrene. These were mixed in a Brabender at 325 F at different ratios with polylactic acid.

The polystyrene/polylactic acid ratios used were 100/0 for the control, and 90/10, and 75/25 for the Huntsman 208, general purpose  
5 polystyrene.

#### Examples 6C-7C

Two types of polyethylene terephthalate were used. (Goodyear's "Clearstuff" and Eastman's Kodapak TN-0148). These were dried overnight at 90 C and melt blended at 525 F in a Brabender with  
10 polylactic acid for only a few minutes. The polylactic acid reduced the melt viscosity.

#### Examples 8C-16C

The controls and blends for polypropylene, general purpose polystyrene, and polyethylene terephthalate (Eastman's) from Examples  
15 2C-7C were ground in an Abbey grinder and compression molded into approximately 5 mil films. Polypropylene-polylactic acid films were molded at about 400 F; polystyrene-polylactic acid films were obtained at 250-300 F; polyethylene terephthalate-polylactic acid films were molded at about 525 F. After conditioning at 50 percent r.h. and 23 C  
20 for 24 hours they were tested on the Instron. The controls were similarly treated. Samples of the compression molded film were placed in an Atlas Weather-O-Meter for weatherability evaluation (cycles of 102 minutes of sunshine and 18 minutes of rain). The results for these Examples are shown in Table 1C.

#### 25 Examples 17C-19C

Three samples of 100 percent polylactic acid using poly (D,L-lactic acid) were prepared as above but with film thicknesses of 10-15 mil. Tests were performed as in Examples 20C-27C below except that the second sample was tested after 82 hours of exposure to 50 percent  
30 relative humidity at 72 F.

Examples 20C-27C

High density polyethylene, HDPE, (0.960 g/cc) was melt blended with polylactic acid in the Brabender Plasticorder at 151 C for 10 minutes. Blend ratios of high-density polyethylene/polylactic acid of 100/0 for the controls, 90/10, 80/20, and 50/50 were used. Two samples of each were prepared. The blends were ground in an Abbey grinder and compression molded into 10-15 mil films. The films were tested in an Atlas Weather-O-Meter set for 51 minutes of carbon arc light and 9 minutes of water spray. Temperature was varied from ambient to 140 F. Tensile strengths, elongation to yield tests and classification of the tensile failure were performed for the samples as shown in Table 2C.

Examples 28C-33C

Low density polyethylene, LDPE, (0.917 g/cc) was melt blended with polylactic acid in the Brabender Plasticorder at 151 C for 10 minutes. Blend ratios of low density polyethylene/polylactic acid of 100/0 for the controls 90/10 and 50/50 were used. Two samples of each were prepared. The samples were treated and evaluated as in the case of Examples 20C-27C. Results are shown in Table 2C.

Example 34C

In a 500-ml, 3-neck, round bottom flask, equipped with a mechanical stirrer and a nitrogen inlet and outlet, was placed 180.7 g. of L-lactide and 40.2 g of racemic D,L-lactide (both Boehringer and Ingelheim, grade S). The contents of the flask were heated to 110 C under a nitrogen sweep to melt the lactides and 20.1 g of polystyrene (Amoco R3, melt index 3.5 g/10 min.) was added. The polystyrene swelled highly and partially dissolved while stirring overnight and advancing the heat to 185 C. The temperature was decreased to 141 C and 0.2 ml of anhydrous stannous octoate solution (0.2 ml/ml of toluene) was added. The stirrer was turned off and the lactides allowed to polymerize at 141 C over 3 days time. The highly swollen, polystyrene floated to the top after turning off the stirrer. The lower, polylactide phase was cooled and examined by differential scanning calorimetry (DSC). The sample has a low Tg, approximately 35

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C, and is otherwise lacking in apparent temperature transitions. Compression-molded films are clear, colorless, and very pliable. These results indicate that the polystyrene thoroughly interrupts crystallinity formation under these conditions.

#### 5 Example 35C

Poly(lactic acid) was mill roll blended with crystal polystyrene. The blend revealed excellent compatibility of polystyrene dispersed in poly(lactic acid). Thus 5 weight percent of polystyrene was dispersed in a 90/10 ratio of L-/racemic D,L-lactide copolymer in a two roll mill at 10 170 C. The material became hazy and exhibited considerable crystallinity by thermal analysis. This example demonstrates that under these conditions polystyrene easily induces crystallinity in poly(lactic acid). A thermal analysis of the material, see Figure 13, reveals that the material remains crystalline even when heated and 15 cooled.

The Examples 34C and 35C illustrate that poly(lactic acid) blended with the environmentally nondegradable plastics herein can produce final properties in the mixture depending on the mixing or blending technique used.

20 Brabender melt-blends of all types exhibited small heterogeneous particle sizes of 10 microns or less. The tensile strengths were evaluated before, and after, simulated weathering. After 1248 hours (52 days) in the Atlas Weather-O-Meter all of the polypropylene samples were whitened, extremely brittle and were not able to be tested. The 25 polypropylene samples were retested at shorter intervals as shown in Table 1C. At approximately 300 hours of weathering in the Atlas Weather-O-Meter, the samples exhibited significant environmental degradation.

The polystyrene blends with poly(lactic acid) exhibited 30 environmental degradation that was apparent after 300 hours of simulated weathering. The poly(ethylene terephthalate) blends were also visibly environmentally degraded in approximately 300 hours.

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TABLE 1C. TENSILE STRENGTH OF FILMS BEFORE, AND AFTER ACCELERATED WEATHERING(a)

5	Blend Ratio and Material	Tensile Strength <sup>(b)</sup> /% Elongation		
		Before	After, hrs 310      400	
	100/0 PP/PLA(c)	1665/61	585/1.6	494/1.7
	90/10, PP/PLA	1568/51	954/3.2	346/--
10	75/25, PP/PLA	1124/14	370/1.1	254/1.0
	100/0 PP/PLA(d)	3200/2.0	1066/1.0	--
	90/10, PS/PLA	2350/2.0	582/1.0	--
	75/25, PS/PLA	1493/1.6	484/1.0	--
	100/0 PET/PLA(e)	3036/--	3509/3.0	--
15	90/10, PET/PLA	2147/--	1378/3.0	--
	75/25, PET/PLA	2743/--	2041/3.0	--

(a) Weather-o-meter, cycle of 102 minutes of sunshine, 18 minutes of rain.

20 (b) 0.05 in./min., on the Instron.

(c) Hercules polypropylene 825.

(d) Huntsman 208.

(e) Tennessee Eastman, Kodapak TN 0148.

25 The polylactic acid, high density polyethylene, low density polyethylene, and their blends were evaluated for physical strength, before, and after simulated weathering and the results are shown in Table 2C.

TABLE 2C. PHYSICAL PROPERTIES OF POLYETHYLENE (PE), POLYLACTIC ACID (PLA), AND THEIR BLENDS, BEFORE, AND AFTER, WEATHER-O-METER EXPOSURES

	Material (a)	Material Blend Ratio (b) Polymer/PLA	Weather-O-Meter (c) Exposure, hours	Tensile Strength, psi	Elongation (d) to Yield, %	Type of Tensile Failure
5	100% PLA (e)	0/100	0	6,030	2.2	Brittle
	100% PLA	0/100	0 (f)	5,670	2.1	Brittle
	100% PLA	0/100	82	(too brittle to test)	--	Brittle
	100% HDPE (g)	100/0	0	3,540	8	Ductile
10	100% HDPE	100/0	233	1,400	1	Brittle
	HDPE/PLA	90/10	0	3,480	7	Ductile
	HDPE/PLA	90/10	233	1,720	1	Brittle
	HDPE/PLA	80/20	0	3,180	4	Brittle
15	HDPE/PLA	80/20	125	2,150	2	Brittle
	HDPE/PLA	50/50	0	2,720	2	Brittle
	HDPE/PLA	50/50	233	(too brittle to test)	--	Brittle

a) Compression-molded films, 10-15 mil thickness.

b) Melt-blended in Brabender Plasticorder for 10 minutes, 151 C.

c) 51 minutes of carbon arc light and 9 minutes of water spray for each 1 hour cycle. Temperature varies from ambient to 140 F.

d) Elongation at maximum in strain curve.

e) Poly(D,L-lactic acid),  $\{\eta\} = 1.16$  dl/g, 25 C, THF.

f) After 82 hours exposure to 50% R.H., 72 F.

g) High density polyethylene, density 0.960 g/cc, melt index 0.6 g/10 minutes.

TABLE 2C. PHYSICAL PROPERTIES OF POLYETHYLENE (PE), POLYLACTIC ACID (PLA),  
AND THEIR BLENDS, BEFORE, AND AFTER, WEATHER-O-METER EXPOSURES

(CONTINUED)	Material (a)	Material Blend Ratio (b) Polymer/PLA	Weather-O-Meter (c) Exposure, hours	Tensile Strength, psi	Elongation (d) to Yield, %	Type of Tensile Failure
5	100% LDPE (h)	100/0	0	1,320	80	Ductile
	100% LDPE	100/0	125	1,250	67	Ductile
	LDPE/PLA	90/10	0	1,190	31	Ductile
	LDPE/PLA	90/10	125	855	14	Ductile
	LDPE/PLA	50/50	0	1,160	4	Ductile
10	LDPE/PLA	50/50	125	(too brittle to test)	--	Brittle

- a) Compression-molded films, 10-15 mil thickness.  
b) Melt-blended in Brabender Plasticorder for 10 minutes, 151 C.  
c) 51 minutes of carbon arc light and 9 minutes of water spray for each 1 hour cycle. Temperature varies from ambient to 140 F.  
d) Elongation at maximum in strain curve.  
h) Low density polyethylene, density 0.917 g/cc, melt index 0.25 g/10 minutes.

The polylactic acid and its blends were much more environmentally degradable than the pure low density or high density polyethylene. The high density polyethylene samples degraded substantially without weight loss while the high density polyethylene-polylactic acid blends  
5 exhibited weight loss, particularly where microscopy revealed polylactic acid was exposed at the surface of the films. The high density polyethylene degraded by exposure to actinic light as shown by microscopy.

With all of the samples, increasing the percentage of polylactic  
10 acid decreased the tensile strength before, and after, simulated weathering. The incorporation of polylactic acid introduced a faster degradation in blends of polypropylene, polystyrene, polyethylene terephthalate, and high and low density polyethylene. Presumably, the actinic light as well as hydrolysis of the polyesters degrades the  
15 polymer. The small size of the spherical, microheterogeneous, domains of the blend are undoubtedly polylactic acid, which is mostly buried. Therefore, polylactic acid hydrolysis is slow. Faster degradation via hydrolysis can be achieved by controlling the location of the polylactic acid. This, in turn, is related to the rheology of the  
20 blend during melt blending. The small size of the dispersed, heterogeneous domains indicates good compatibility of the mixed polymers.

In a simulated landfill, where light is excluded, the controls and the blends show much slower rates of degradation. With hydrolysis, alone, the polylactic acid samples slowly whiten, while the blends are  
25 qualitatively unchanged for the time period tested.

Conversely, addition of minor amounts of nondegradable thermoplastics to polylactic acid to form compatible blends, using, for example, polypropylene, polystyrene, polyethylene terephthalate and high and low density polyethylene will retard the degradation rate of  
30 the polylactic acid. A preferred compositional range is from 80-99 weight percent polylactic acid.

A general description of the environmentally degradable composition comprises blends of a physical mixture of polylactic acid (polylactide), and a polymer selected from the group consisting of a  
35 polymer of ethylene terephthalate, a polymer or copolymer of styrene,

ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. Other possible compositional blends are listed below in the discussion of process embodiments of the invention.

- 5       The blends preferably use a physical mixture of polylactic acid of formula I, where n is an integer between 75 and 10,000; and a polymer selected from the group consisting of polystyrene, polyethylene, polyethylene terephthalate, and polypropylene and other compositions further discussed below. A preferred composition is that where the  
10       polylactic acid comprises 5 to 50 weight percent of the composition. A preferred composition has a polylactic acid content of 10 to 20 weight percent.

- The polymers selected from the group above, deemed the added polymer, can be used alone or in combination. The group is not  
15       restricted to those cited above since other polymer types are noted as compatible with polylactic acid. These include the polymers and copolymers comprised from the group of ethylene, propylene, styrene, vinyl chloride, vinyl acetate, alkyl methacrylates, and alkyl acrylates. It should be understood that the term copolymers as used  
20       herein includes polymers made from mixtures of the monomers in the listed group. Physical mixtures of the polymers and copolymers of the above group are likewise useful in the invention.

- The third embodiment further provides for a process for producing the composition includes providing a polylactic acid; selecting a  
25       polymer from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and blending the polymers. The blending may be by melt blending on a mill roll or by compounding in an extruder or  
30       by other mechanical means. The polylactic acid provided preferably has the formula I.

- It further provides for a process for producing the composition of the invention includes providing a lactide selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-  
35       lactide, and mixtures thereof; selecting a polymer from the group

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- consisting of the polymers or copolymers of styrene, ethylene, ethylene terephthalate, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof. The selected lactide and polymer are mixed and heated to melt the lactide and at least partially dissolve the polymer. Finally, the lactide, is at least partially polymerized to obtain a blend of polylactide, unpolymerized lactide monomer and the selected polymer. The polymerization is preferably controlled by monitoring the amount of lactide remaining and stopping the polymerization at the desired level.
- 10 If desired, the polymerization can be carried to completion. Additional lactide monomer, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof in pliable producing amounts can be added as plasticizers to obtain desired characteristics as taught in the first general embodiment.
- 15 It will be obvious to those skilled in the art that the proportions of polylactic acid and the added polymer can vary widely depending on their mutual solubilities. Solubilities, in turn, vary with the thoroughness of mixing and the mixing temperature. While placing both the polylactic acid and the added polymer into a mutual
- 20 solvent solution will obtain intimacy, the use of solvent is impractical for many commercial processes. Physical mixing, such as melt blending on a mill-roll or extruder is more practical, but must be controlled to achieve intimacy, that is, high shear is required to achieve the desired intimacy. Even with intimate mixing different
- 25 polymers may not be compatible, that is, they may still separate into relatively large heterogeneous domains of, for example, 10 to 100 micron size, or larger. This results in a "cheesy" mixture, or a blend with poor properties. What is surprising is that polylactic acid is easily blend compatible with a wide variety of other polymers,
- 30 including both polar and nonpolar polymers.

The temperature of the melt blending of the polylactic acid with other polymers may be varied to adjust the proportions of the polylactic acid with one, or more, added polymers. At lower temperatures, the solubilities may not be adequate, while too high a

35 temperature will cause decomposition of the mixture. A general

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temperature range is 100 - 220 C, and the preferred range is 130 - 180 C. Equally significant is the melt viscosities of the different polymer components. With increasing molecular weight, the viscosities increase sharply. By controlling the proportions of the polylactic acid and the added polymer, or polymers, the temperature, the mixing type and time, and the molecular weight, a wide range of mixtures can be obtained. Thus, for example, the polylactic acid can be dispersed into the added polymer, or polymers, or vice versa, and the size and geometry of the dispersed phase varied greatly, ranging from discrete spheres to strands of different diameters or lengths. This results in a wide latitude of physical properties and degradation times in the environment. The weight percent ratio of polylactic acid to the selected polymer can be between 99:1 to 1:99.

Where the lactide monomer is used to dissolve the added polymer and the lactide is subsequently polymerized, the temperature of mixing and polymerizing must be balanced between the mutual solubilities and the reactivity of the lactide. Higher temperatures generally produce lower molecular weight polylactic acid. A further embodiment of the invention is to mix at one temperature and polymerize at another temperature to achieve variations in the geometry of the dispersed phase, as discussed above.

The compositions herein can be processed by melt fabrication into useful articles of manufacture having a self supporting structure such as disposable containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, packaging films and the like. The compositions are useful in that they can have the characteristics of the usual plastics and therefore substitute for them yet degrade in the environment. The compositions are especially useful for articles having only a one time use or a short life span in use before disposal.

#### Fourth General Embodiment

Within the fourth embodiment of the invention are included those impact modifiers which are elastomeric and melt compatible with polylactic acid. By "melt compatible", it is meant all those polymers

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which can be intimately mixed with polylactic acid as discussed in the third general embodiment. The mix would result in a substantially homogeneous blend.

The environmentally degradable compositions disclosed herein are at least partially degradable. That is the polylactic acid portion of the composition will decompose relatively rapidly compared to the more stable portions of the blend and cause a physical deterioration of the blended material. For example, when the compositions are intimate and homogeneous blends with small domain sizes the physical deterioration will destroy the original formed product. The compositions herein provide environmentally acceptable materials because their physical deterioration and degradation is much more rapid than conventional nondegradable plastics. Further, since a major portion of the composition will be polylactic acid, and/or a lactic acid derived lactide or oligomer only a small portion of more slowly degrading elastomer residue will remain (e.g. segmented polyester). This residue will have a high surface area and is expected to decompose faster than a bulk formed product.

The examples below show the blending of polylactic acid (PLA) with a Hytrel™, a segmented polyester which is a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long-chain segments of polyether glycol. It is shown that polylactic acid is melt compatible with this elastomer and the effect on its physical properties.

D-lactide is a dilactide, or cyclic dimer, of D-lactic acid. Similarly, L-lactide is a cyclic dimer of L-lactic acid. Meso D,L-lactide is a cyclic dimer of D- and L-lactic acid. Racemic D,L-lactide comprises a 50/50 mixture of D-, and L-lactide. When used alone herein, the term "D,L-lactide" is intended to include meso D,L-lactide or racemic D,L-lactide. Polylactic acid may be prepared from one or more of the above.

#### Example 10

A polylactide copolymer without Hytrel™ segmented polyester was prepared using the procedure from Example 1B of the second general

embodiment of Serial No. 229,939 and tested for Izod impact strength. Results are shown in the Table 1D. For further comparison, Table 1B of the second general embodiment lists the Izod impact strength of other ratios of L-lactide to D-L lactide.

#### 5 Example 2D

Into a 3-neck, 250 ml, round-bottom flask is weighed 10.96 g of D,L-lactide, 108.86 g of L-lactide, and 5.27 g of Hytrel™ 4056 segmented polyester (Du Pont, a thermoplastic elastomer). Hytrel™ 4056 segmented polyester is a polyester elastomer with a Shore D durometer, 10 low flexural modulus, high melt viscosity, a melt index of 7, a sp. gr. of 1.17, a m.p. 334 F, a vicat softening temperature of 234 F, and an extrusion temperature of 340 F - 400 F. The flask is fitted with a mechanical stirrer and a nitrogen inlet and outlet. The contents are heated by means of an oil bath. The Hytrel™ segmented polyester dis- 15 solves in the molten lactides at 170 C. A catalyst solution is prepared by dissolving 10 ml of stannous octoate in 60 ml of toluene and distilling 10 ml into the toluene. A 100 microliter portion of the catalyst solution is injected into the solution of lactide and Hytrel™ segmented polyester. The mixture is stirred under nitrogen at 155 C 20 for approximately 64 hours.

The viscosity increases sharply and the mixture turns cloudy. The product is tough and opaque. Films of 8-9 mil thickness were compression molded at 155 C and the tensile properties measured, as shown in Table 1D.

25 Slabs, 1/8 inch thick, were compression molded and their Izod impact strength measured using a 2 pound pendulum. The results are recorded in the Table 1D where the data are compared to a similar polylactide copolymer of Example 1D without Hytrel™ segmented polyester, and to data for so-called medium-impact polystyrene, Example 30 7D.

#### Example 3D

800.0 g of L-lactide and 202.3 g of racemic D,L-lactide are copolymerized using 1.0 ml of the catalyst solution by methods similar

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to Example 2D, omitting the Hytrel™ segmented polyester. The lactide copolymer is clear and colorless. In a separate polymerization 104.0 g of L-lactide is melt polymerized using 100 microliters of catalyst. The polymer (L-PLA) is white, crystalline, and crazes easily when struck.

An electrically-heated, 2-roll mill is heated to 375 F, then 8.4 g of Hytrel™ segmented polyester and 19.2 g of L-PLA are banded on the roll. To this was added 172.4 of the lactide copolymer. The mixture blends easily and is removed from the rolls, molded, and tested as in Example 2D. The data are recorded in Table 1D.

#### Example 4D

The lactide copolymer of Example 3D, 80 g, the L-PLA of Example 3D, 10 g, and 10 g of Hytrel™ 4056 segmented polyester are 2-roll, mill-blended as described previously in Example 3D. The blend was tested as before and the data are recorded in Table 1D.

#### Example 5D

100 g of the blend of Example 3D was further blended with 20 g of Hytrel™ 4056 segmented polyester. The mixture easily mixed on the roll and was apparently quite compatible. The physical properties were measured as described previously and recorded in Table 1D.

#### Examples 6D and 7D

Typical crystal polystyrene and medium-impact polystyrene were tested and used for comparative controls.

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The above results clearly indicate that polylactides can be impact-modified. The blends provided significantly higher Izod impact strengths than the crystal polystyrene control and gave slightly lower or equivalent impact strengths compared to medium-impact polystyrene. Those skilled in the art will recognize that the data on impact-strength in Table 1D can be improved further by optimizing the amount and type of impact modifier.

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Since polylactides have been shown previously in the third general embodiment above, to be blend-compatible with numerous other compounds and thermoplastics, the process of impact-modifying polylactides is generic to mixtures of polylactides and elastomers that are blend-compatible. Also, those skilled in the art will recognize that the data of the Table 1D will improve as the blends are injection-molded, as opposed to compression-molded, since the former often induces orientation of the specimens and, consequently, a profound improvement in impact strength.

TABLE 1D.  
PHYSICAL PROPERTY COMPARISONS OF IMPACT-MODIFIED POLYLACTIDES

Example No.	Composition, weight percent		Tensile Strength, psi(b,c)	Elongation, percent	Tangent Modulus, psi	Izod Impact Strength ft-lb/in.(c)
	Lactide Copolymer	L-lactide Homopolymer Hytrel™(a)				
10	80(d)	20	7,667	3.4	322,679	0.3-0.4
20	95.8(e)	0	8,636	3.1	359,409	0.40
30	86.2(g)	9.6	7,823	3.1	346,502	0.51
40	80.0(g)	10.0	---	---	---	0.53
50	71.2(g)	7.9	---	---	---	0.61
60(i)	0	0	6,118	3.2	267,245	0.18
70(j)	0	0	6,090	4	---	0.7

(a) DuPont Hytrel™ 4056, a thermoplastic polyester elastomer.  
(b) ASTM D 882, 7-15 mil film thickness.

15 (c) Compression-molded specimens.

(d) control, 90/10, L-D/L-lactide copolymer.  
(e) 91/9, L-D/L-lactide copolymer.

(f) Hytrel™ dissolved in lactide monomers before 170 C polymerization.

20 (g) 80/20, L-D/L-lactide copolymer.  
(h) 2-Roll mill-blend at 185-190 C.

(i) Control, crystal polystyrene, melt-index 1.7.  
(j) Control, medium-impact polystyrene

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The compositions are useful thermoplastics that can be melt fabricated by conventional processes such as extrusion and molding.

The blends preferably use a physical mixture of polylactic acid of formula I, where  $n$  is an integer between 75 and 10,000; and a polymer comprising a segmented polyester. A useful composition is that where the polylactic acid comprises 50 to 99 weight percent of the composition. A preferred composition has a polylactic acid content of 70 to 80 weight percent.

Two embodiments of the general process for producing the composition include (1) melt blending of PLA with a blend compatible polymer that provides improved impact resistance such as a segmented polyester and (2) solution blending during PLA polymerization as in Example 2D where Hytrel™ segmented polyester is dissolved in the PLA. The polylactic acid provided preferably has the formula I. If desired plasticizer in pliable forming amounts may be added to the blend that is selected from the group consisting of lactide monomer, lactic acid oligomer, lactic acid, and mixtures thereof. Addition of the plasticizer will provide additional unique physical properties as discussed in the first, second, and third general embodiments discussed above.

Microscopic examination of the Hytrel™ segmented polyester/polylactic acid mixture revealed that the dispersed Hytrel™ segmented polyester is present in small spherical domains a few microns or less in size. These domain sizes can be adjusted by the mixing conditions such as time, speed of mixing, and temperature.

Therefore, for example, the polymer, or polymers, added to the polylactic acid, should be generally of small, heterogeneous domain size, less than 10 microns, and can be submicroscopic, or dissolved, in the polylactic acid. In addition, this impact modifier must be elastomeric.

While not wishing to be held to any particular theory, it is believed that the present invention provides a continuous matrix of polylactic acid containing intimately mixed microscopic domains of Hytrel™ segmented polyester that act as crack arrestors since the latter is a thermoplastic elastomer compatible with polylactic acid.

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For this purpose, the impact modifier must be elastomeric and intimately bound into the polylactic acid as a discrete heterogeneous phase. The added polymer, the impact modifier, can be a thermoplastic elastomer, or a crosslinked rubber, to achieve this elastic behavior.

5 Examples are natural rubber and styrene-butadiene copolymers.

In a test of material placed in water for five months, the material embrittled compared to a material not exposed to water. In addition the water turned acidic indicating breakdown of polylactic acid to lactic acid. It was further apparent that polylactic acid  
10 alone degraded faster than the Hytrel™ segmented polyester/polylactic acid mixture. Thus Hytrel™ segmented polyester can also be used to retard the degradation rate of polylactic acid.

A third component can be added which is compatible with the other components discussed above to achieve improved compatibility. Thus,  
15 where the polylactic acid and the impact modifier have poor compatibility, a third component can be added to improve the compatibility. This third component is usually added where it is compatible with the other two, individually, and where the other two, polylactic acid and impact modifier are not very compatible. This  
20 works by increasing the interfacial bonding between polylactic acid and elastomeric impact modifier. However, what is surprising is the wide latitude of compatibility of polylactic acid with other polymer types, both polar and nonpolar. This can be referred to in the third general embodiment.

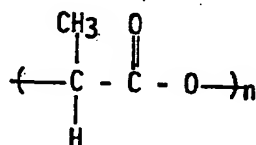
25 The compositions herein can be processed by melt fabrication into useful articles of manufacture such as containers, eating utensils, trays, plates, drinking cups, single serving trays, syringes, medical trays, and the like. The compositions are especially useful for articles having only a one time use or a short life span in use before  
30 disposal.

While the invention has been described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such illustrated examples and embodiments and may be variously practiced within the scope of the claims  
35 hereinafter made.

CLAIMS

We claim:

1. An environmentally biodegradable composition useful as a replacement for thermoplastic polymer compositions comprising a polymer  
5 of the formula:

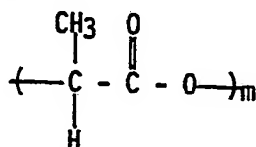


that is plasticized with a plasticizer selected from the group  
10 consisting of lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof, wherein n is the number of repeating units and n is an integer,  $150 \leq n \leq 20,000$ , and the unoriented composition has a tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi.

- 15 2. The composition of Claim 1, wherein the polymer is derived from monomers of lactide selected from the group consisting of L-lactide, D-lactide, meso D,L-lactide, and mixtures thereof.

3. The composition of Claim 1, wherein the oligomers of lactic acid or lactide have the formula:

20



where m is an integer:  $2 \leq m < 75$ .

4. The composition of Claim 1 further comprising additional  
25 plasticizer dispersed within the composition that is selected from the group of monomers consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof such that at least part of the dispersed monomer is stereochemically different from that used to prepare the polymer.

5. The composition of Claim 1 further comprising an oligomer dispersed within the composition which is not produced during polymerization of the polymer.

6. A process for producing an environmentally biodegradable composition of polylactic acid comprising:

- a. preparing lactide monomer and catalyst;
- b. polymerizing the monomer of step (a) to form a polymer at a temperature sufficiently low to allow the reaction to be stopped prior to complete polymerization;
- 10 c. monitoring the level of monomer in step (b); to determine the amount of monomer remaining; and
- d. stopping the polymerization of step (b) prior to complete reaction at an amount of monomer determined in step (c) so that unreacted monomer in a predetermined amount is trapped in association with the polymer.

7. The process of Claim 6 further comprising:

- e. incorporating additional plasticizer into the composition whereby the plasticizer is further selected from the group consisting of L-lactide, D-lactide, meso D,L-lactide, lactic acid, oligomers of lactide, oligomers of lactic acid, and mixtures thereof.

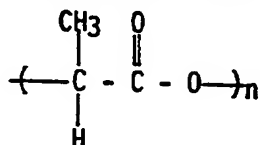
8. The process of Claim 7 further comprising selecting a monomer stereochemically different from that selected to prepare the polymer.

9. A process for producing a biodegradable composition of polylactic acid comprising:

- a. preparing lactide monomer and catalyst;
- b. polymerizing the monomer of the solution of step (a) to form a polymer; and
- 30 c. incorporating plasticizer into the polymer of step (b), whereby the plasticizer is selected from the group consisting of D-lactide, L-lactide, D,L-lactide, oligomers of lactic acid, oligomers of lactide, and mixtures thereof.

10. In a thermoplastic polymer composition comprising first orientable polymer units, a method for rendering the composition environmentally biodegradable which comprises:

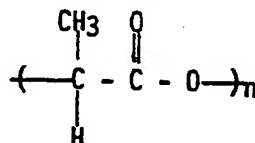
- replacing the first polymer units with a second orientable polymer having an unoriented tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi; wherein the second polymer comprises polylactic acid units of the formula:



- wherein n is the number of repeating units and n is an integer,  $150 \leq n \leq 20,000$  and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide and mixtures thereof.

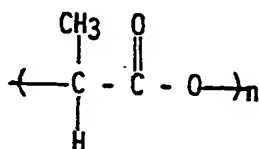
11. In a polyolefin composition comprising first orientable polymer units, a method for rendering the composition environmentally biodegradable which comprises:

- replacing the first polymer units with a second orientable polymer having an unoriented tensile strength of 300 to 20,000 psi, an elongation to failure of 50 to 1,000 percent, and a tangent modulus of 20,000 to 250,000 psi; wherein the second polymer comprises polylactic acid units of the formula:



- wherein n is the number of repeating units and n is an integer,  $150 \leq n \leq 20,000$  and is plasticized with a plasticizer selected from the group consisting of lactide, oligomers of lactic acid, oligomers of lactide and mixtures thereof.

12. An environmentally biodegradable composition useful as a replacement for polystyrene comprising polylactic acid units of the formula:



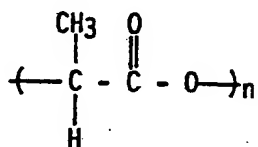
where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units, wherein the polymer is prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight, where the unoriented polymer has a tensile strength of at least 5000 psi and tangent modulus of at least 200,000 psi and dispersed plasticizer of 0.1 - 5 weight percent.

13. The composition of Claim 12 further comprising monomer dispersed within the composition that is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide, and mixtures thereof such that at least part of the dispersed monomer is stereochemically different from the monomer used to prepare the polymer.

14. The composition of Claim 12 further comprising oligomer stereochemically different from that obtained during polymerization of the polymer.

15. An environmentally biodegradable composition useful as a replacement for polystyrene comprising blends of a physical mixture of:

a. a first polymer having polylactic acid units of the formula:



where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D-configurations with a preponderance of either D- or L-units; and

b. a lactide homopolymer of D-lactide or L-lactide; and wherein the unoriented composition has a tensile strength of at least 5000 psi and tangent modulus of at least 200,000 psi and dispersed plasticizer.

16. The composition of Claim 15 further comprising dispersed plasticizer of 0.1 to 5 weight percent.

17. The composition of Claim 15 wherein the polymerized lactic acid is present in an amount of 98 to 75 weight percent and the lactide homopolymer is present in an amount of 2 to 25 percent.

18. The composition of Claim 15 further comprising plasticizer  
5 that is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof.

19. The composition of Claim 15 further comprising plasticizer  
10 that is selected from the group of monomers consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof such that at least part of the dispersed monomer is stereochemically different from that used to prepare the first polymer and homopolymer.

20. A process for producing the composition of Claim 12 comprising:

15 a. mixing with a catalyst, heating, and melting L-lactide or D-lactide monomer, and D,L-lactide monomer whereby the L-lactide monomer or D-lactide monomer is at 85 to 95 parts by weight and D,L-lactide monomer is at 15 to 5 parts by weight, to form an intimate solution;

20 b. polymerizing the solution of step (a); and

c. treating the polymer of step (b) to improve its properties.

21. The process of Claim 20 whereby the treatment comprises adding a D-lactide or L-lactide copolymer by blending.

25 22. The process of Claim 20 whereby the treatment comprises adding a nucleating agent, and a D-lactide or L-lactide polymer by blending.

23. The process of Claim 20 whereby the treatment further comprises:

30 a. controlling the polymerization of step (b) by adding chain transfer agents; and

b. adding nucleating agents and a D-lactide or L-lactide homopolymer by blending.

24. The process of Claim 20 further comprising the step of  
35 treating by adding additional plasticizer to the composition whereby

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the plasticizer is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof.

25. The process of Claim 20 whereby, when a monomer is selected,  
5 at least one monomer is different stereochemically from the monomer(s) selected in step (a).

26. In a thermoplastic polymer composition comprising first orientable polystyrene units, a method for rendering the composition environmentally biodegradable which comprises:

10 replacing the polystyrene units with a second orientable polymer having an unoriented tensile strength of at least 5,000 psi, and a tangent modulus of at least 200,000 psi and dispersed plasticizer of 0.1 to 5 weight percent; wherein the second polymer comprises polylactic acid units of the formula:



where n is an integer between 75 and 10,000 and the alpha carbon is a mixture of L- and D- configurations with a preponderance of either D-  
20 or L- units, wherein the polymer is prepared from L-lactide or D-lactide, at 85 to 95 parts by weight, and D,L-lactide at 15 to 5 parts by weight.

27. An environmentally degradable composition comprising blends of a physical mixture of:

- 25
- a. a polylactic acid; and
  - b. a polymer selected from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof.

30 28. The composition of Claim 27 wherein the weight percent ratio of polylactic acid to the selected polymer is a ratio between 99:1 and 1:99.

29. A process for producing the composition of Claim 27 comprising:

- a. providing a polylactic acid;
  - b. selecting a polymer from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof; and
  - c. blending the polymers of steps a and b.
30. The composition of Claim 27 further comprising plasticizer that is selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, lactic acid, lactide oligomer, lactic acid oligomer, and mixtures thereof.
31. A process for producing an environmentally degradable composition comprising:
- a. providing a lactide monomer selected from the group consisting of D-lactide, L-lactide, meso D,L-lactide, racemic D,L-lactide and mixtures thereof;
  - b. selecting a polymer from the group consisting of a polymer of ethylene terephthalate, a polymer or copolymer of styrene, ethylene, propylene, vinyl chloride, vinyl acetate, alkyl methacrylate, alkyl acrylate, and physical mixtures thereof;
  - c. mixing and heating the lactide selected in (a) and the polymer selected in (b) at conditions adapted to melt the lactide and at least partially dissolve the polymer; and
  - d. polymerizing the lactide in the mixture of step (c) to obtain a blend of polylactide and polymer.
32. The process of Claim 31 further comprising the step:
- e. forming the blend into a self supporting structure.
33. The process of Claim 31 further comprising monitoring the amount of monomer remaining and controlling the polymerization of step (d) to obtain a blend containing residual monomer.
34. The process of Claim 31 further comprising:
- e. adding plasticizer selected from the group consisting of lactide monomer, lactide oligomer, lactic acid oligomer, lactic acid, and mixtures thereof, to the blend after polymerization.
35. An environmentally degradable composition comprising blends of a physical mixture of:

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- a. a polylactic acid; and
- b. a blend compatible polymer that provides improved impact resistance to the polylactic acid.

36. The composition of Claim 35 wherein the polylactic acid  
5 comprises 50 to 99 weight percent of the composition.

37. The composition of Claim 35 wherein the blend compatible polymer is a segmented polyester.

38. The composition of Claim 37 wherein the blend compatible polymer is a block copolymer of hard crystalline segments of  
10 polybutylene terephthalate and soft long chain segments of polyether glycol.

39. A process for producing the composition of Claim 35 comprising:

- a. providing a polylactic acid;
- 15 b. selecting a blend compatible polymer that increases the impact resistance; and
- c. blending the polymers of steps (a) and (b).

40. The process of Claim 39 whereby a segmented polyester is selected.

20 41. The process of Claim 39 whereby a block copolymer of hard crystalline segments of polybutylene terephthalate and soft long chain segments of polyether glycols, or natural rubber and styrene-butadiene copolymers are selected.

42. A process for producing the composition of Claim 35  
25 comprising:

- a. mixing one or more lactides selected from the group consisting of D-lactide, L-lactide, D,L-lactide and mixtures thereof with a blend compatible polymer that provides improved impact resistance to the composition;
- 30 b. heating and dissolving the blend compatible polymer in the lactide(s) of step (a) to form a solution; and
- c. polymerizing the lactide(s) in the solution.

43. The process of Claim 42 further comprising the step of fabricating the composition into useful forms by melt fabrication.

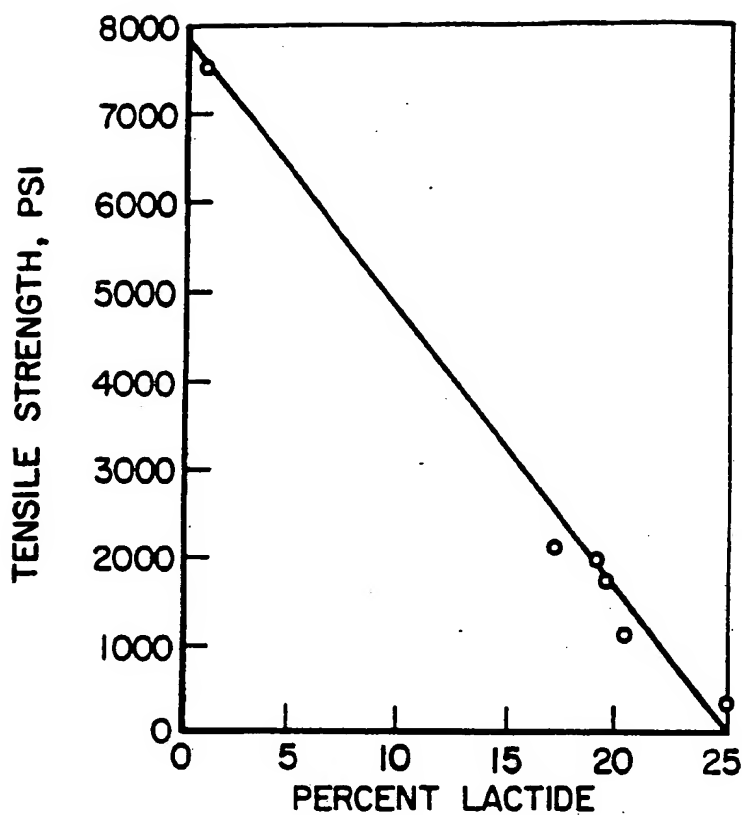
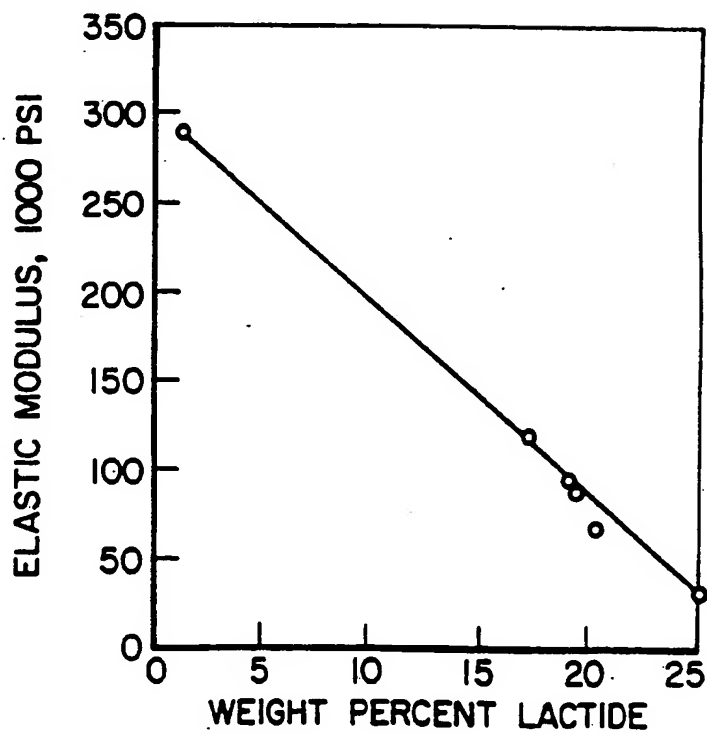
- 92 -

44. The process of Claim 42 further comprising: Selecting a blend compatible polymer that comprises a segmented polyester.

45. The process of Claim 42 further comprises selecting a blend compatible polymer from the group consisting of a block copolymer of  
5 hard crystalline segments of polybutylene terephthalate and soft long chain segments of polyether glycols, and natural rubber and styrene-butadiene copolymers or a mixture thereof.

46. The process of Claim 35 further comprising:

10 e. adding plasticizer to the blend selected from the group consisting of lactide monomer, lactide oligomer, lactic acid oligomer, lactic acid, and mixtures thereof.

**FIG. 1****FIG. 2**

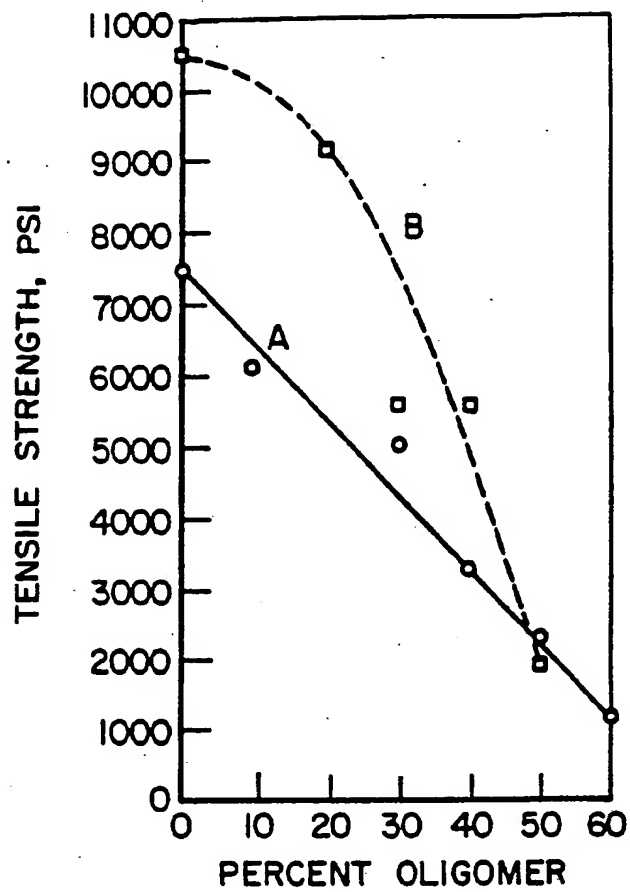


FIG. 3

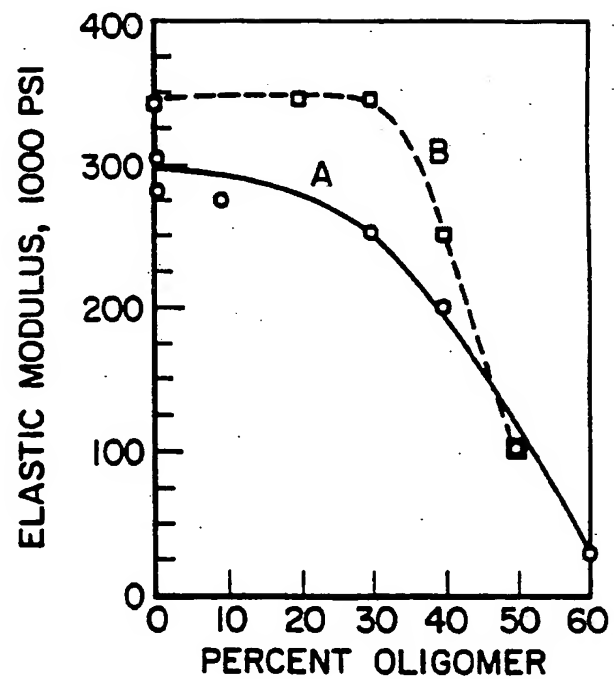


FIG. 4

3

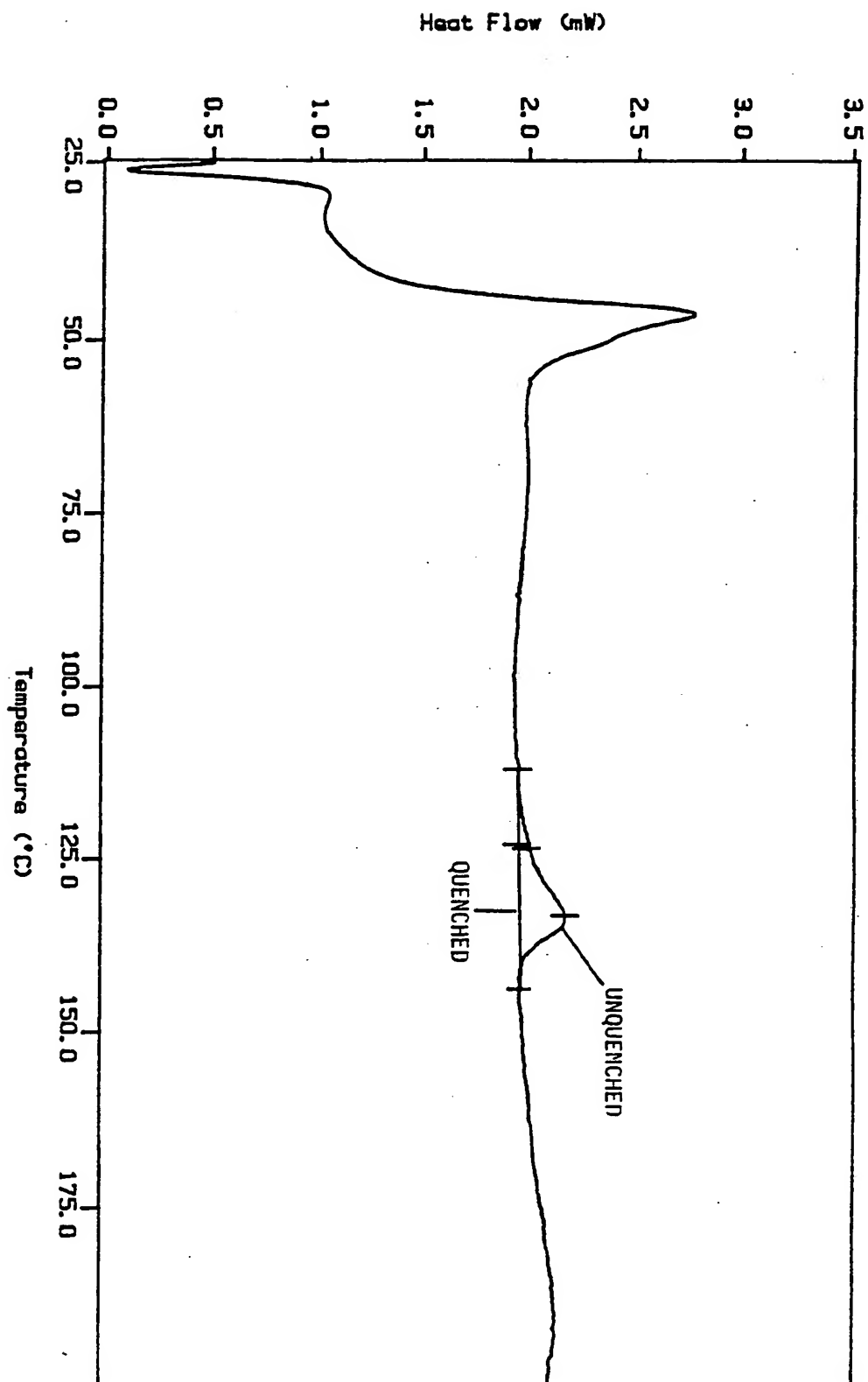


Figure 5. DSC OF UNANNEALED 90/10; L-/D,L-LACTIDE COPOLYMER

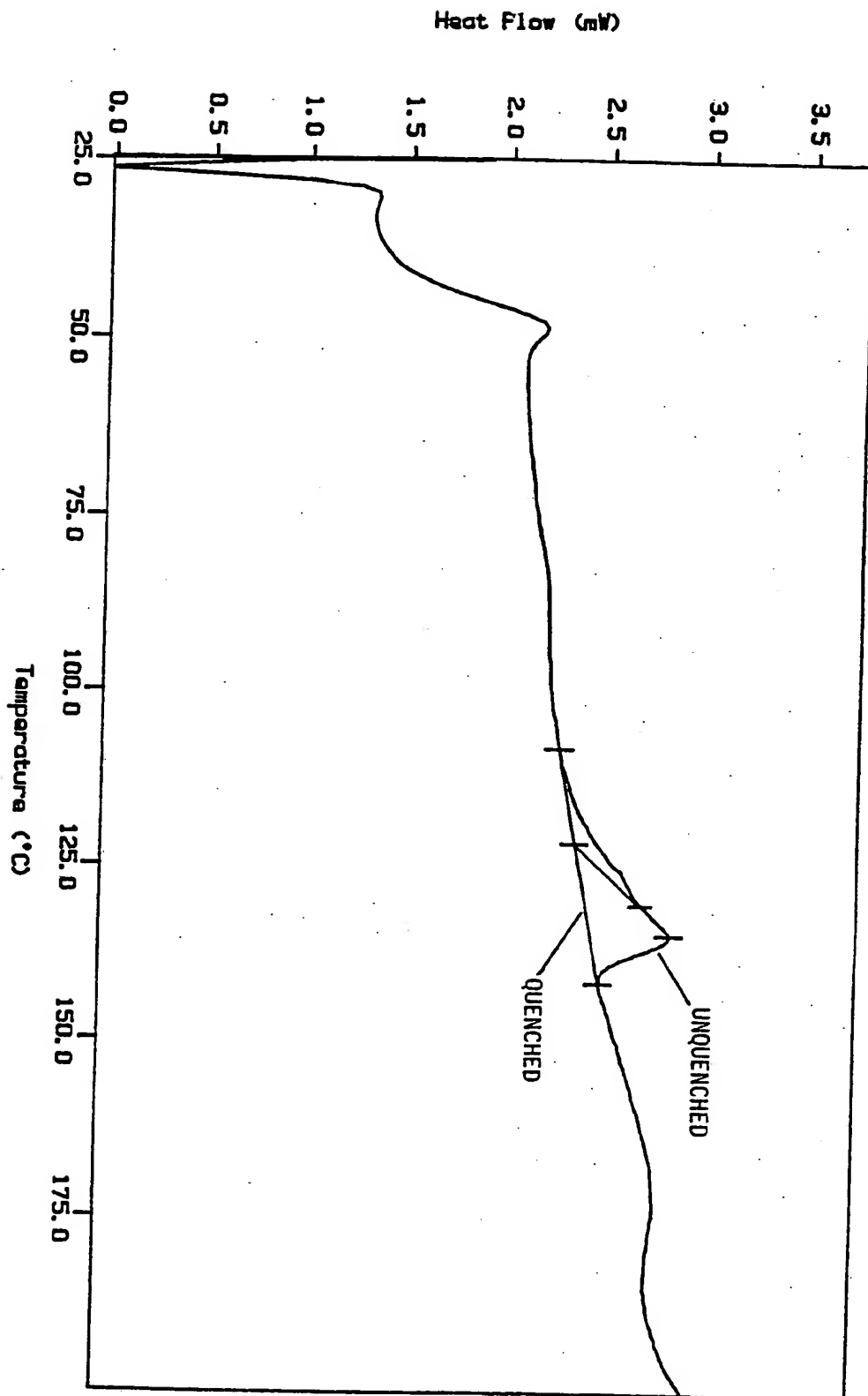


Figure 6. DSC OF SAMPLE OF FIGURE 1 AFTER 100 MINUTES AT 70 C

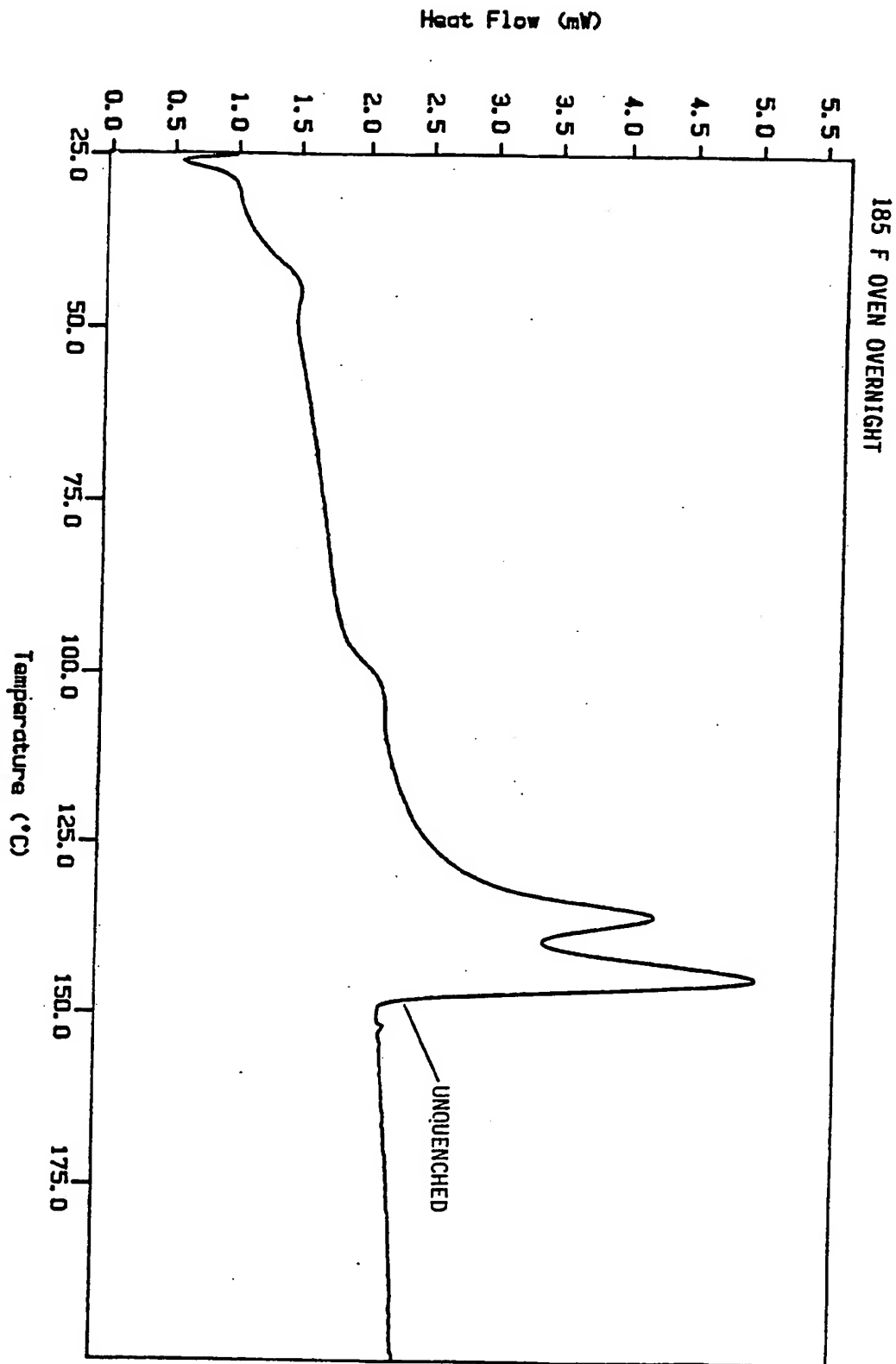


Figure 7. DSC OF ANNEALED COPOLYMER OF FIGURE 1

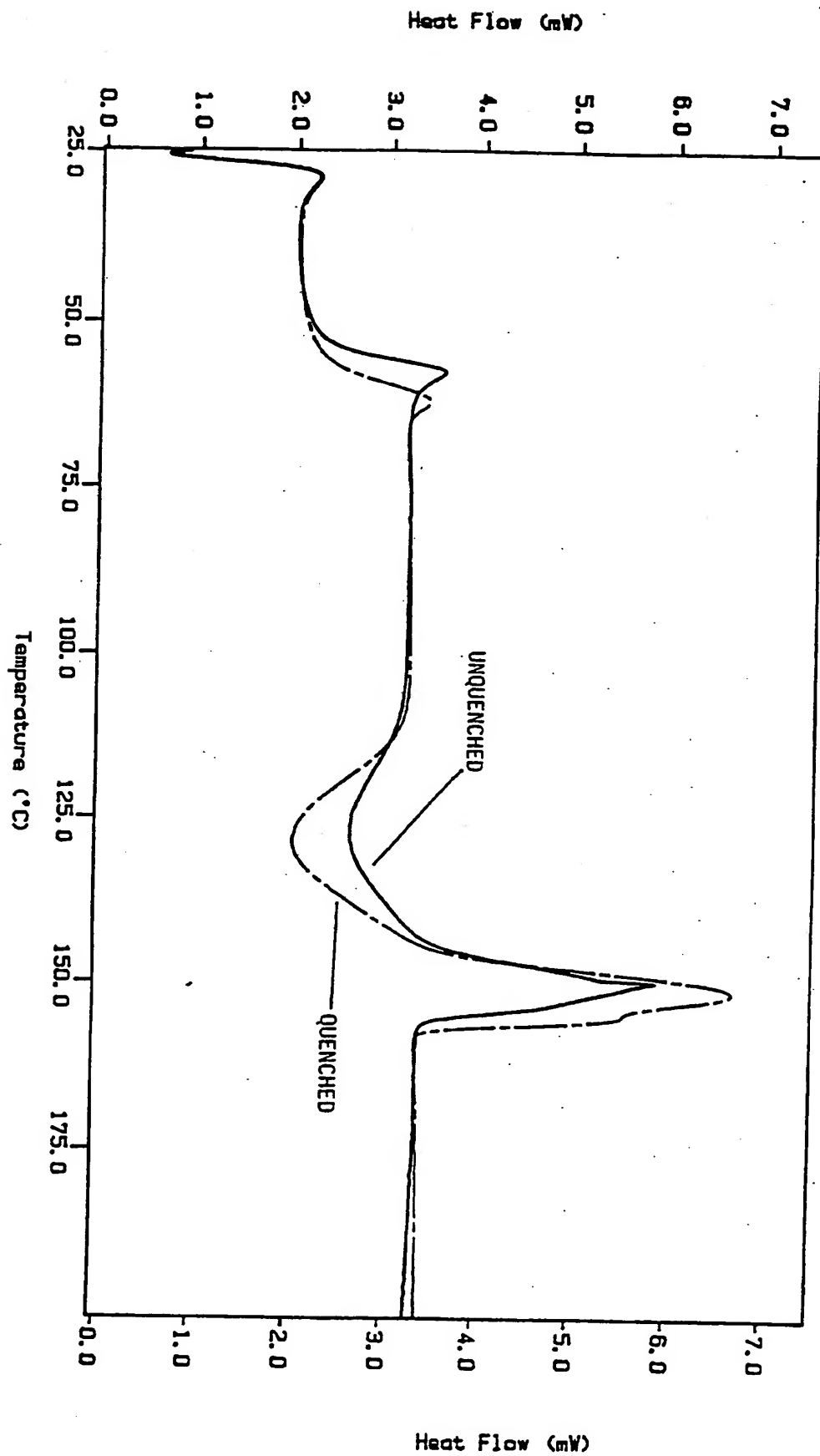


Figure 8. DSC OF 90/10, L-/D,L-LACTIDE COPOLYMER BLENDED WITH 5 PERCENT CALCIUM LACTATE

# VISCOSITY VS SHEAR RATE

Lactide Polymer of Example #8

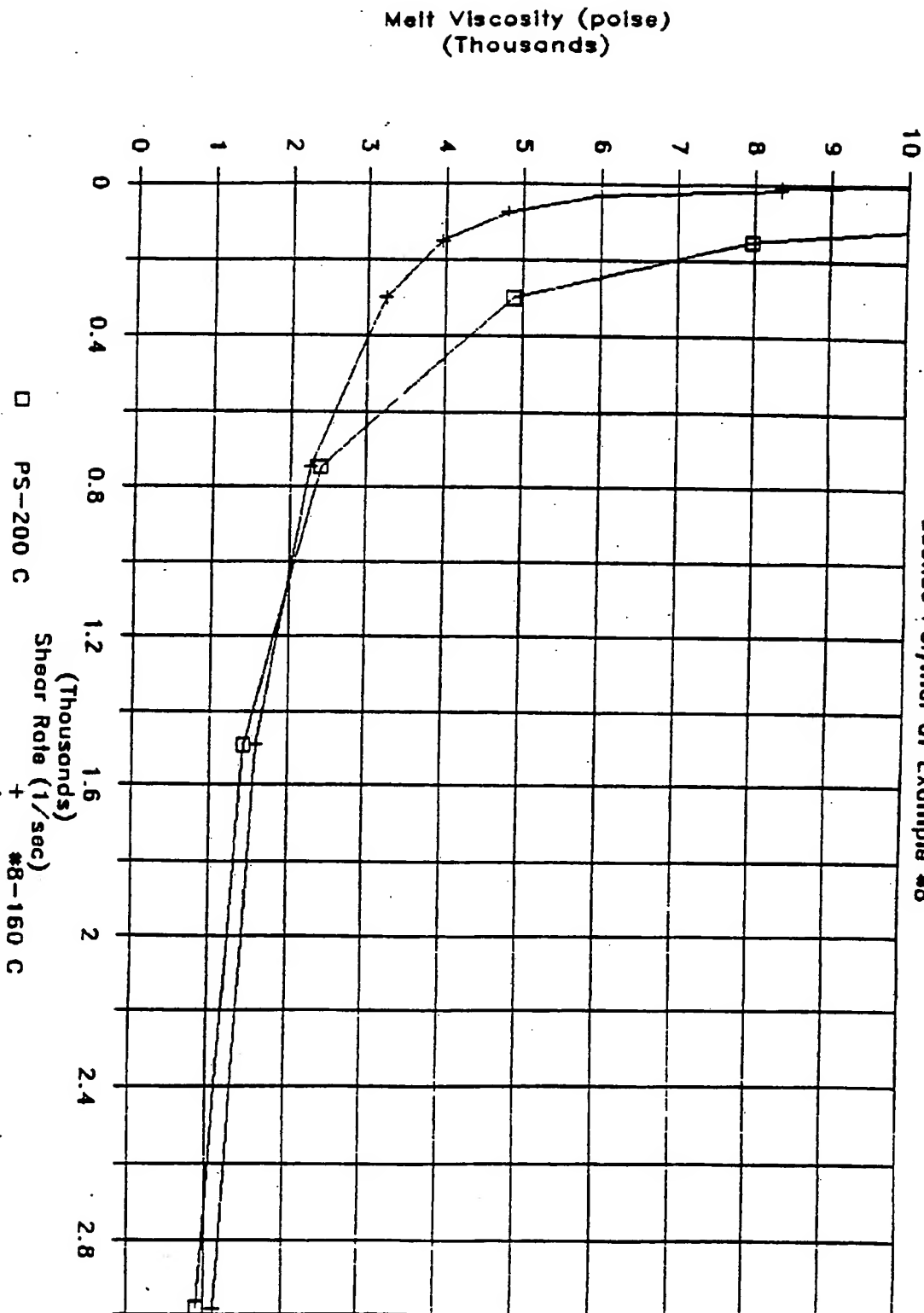


Figure 9. MELT VISCOSITY COMPARISON OF POLYSTYRENE AND LACTIDE POLYMER OF EXAMPLE 8

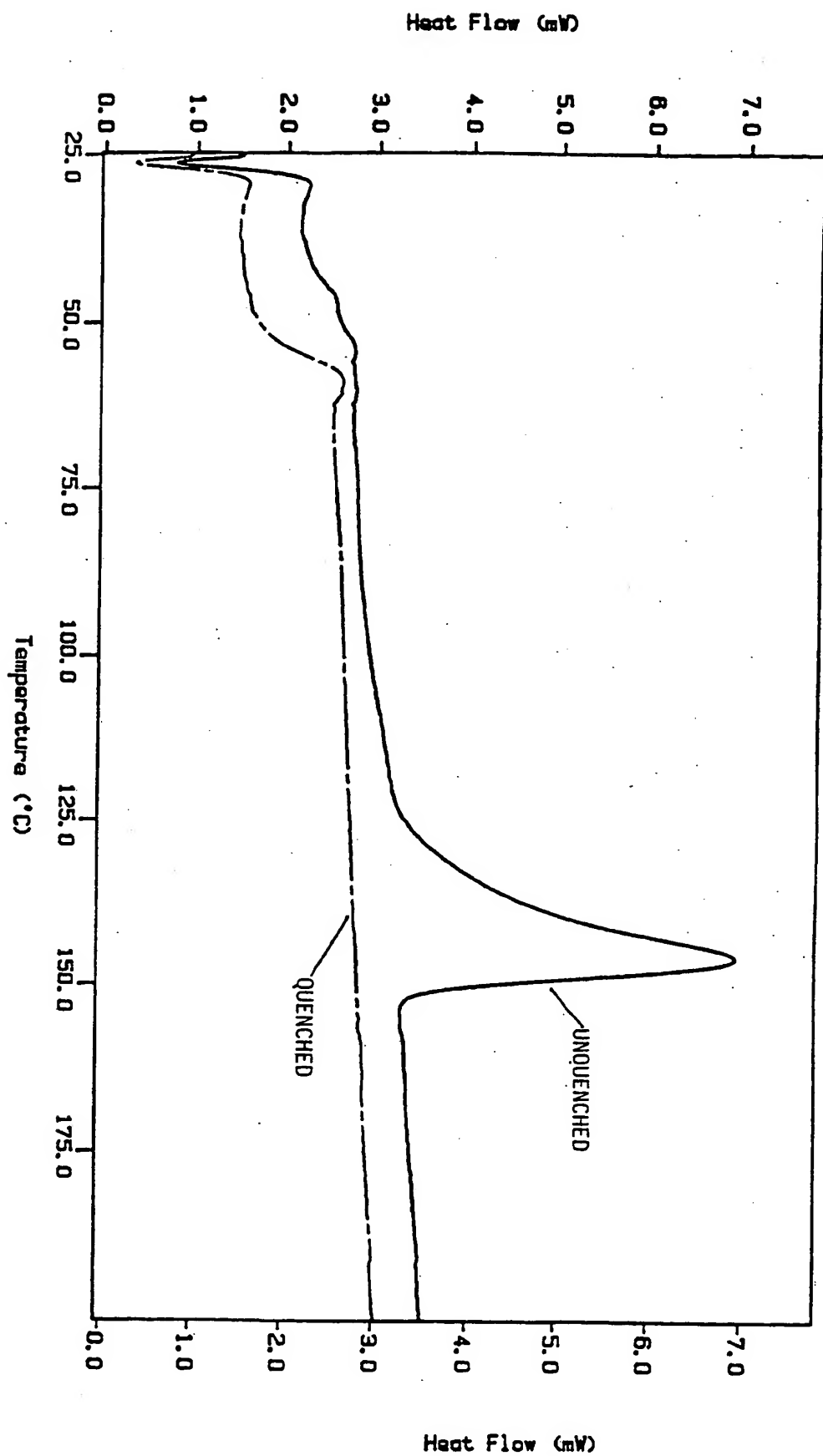


Figure 10. MATERIAL FROM EXAMPLE 8

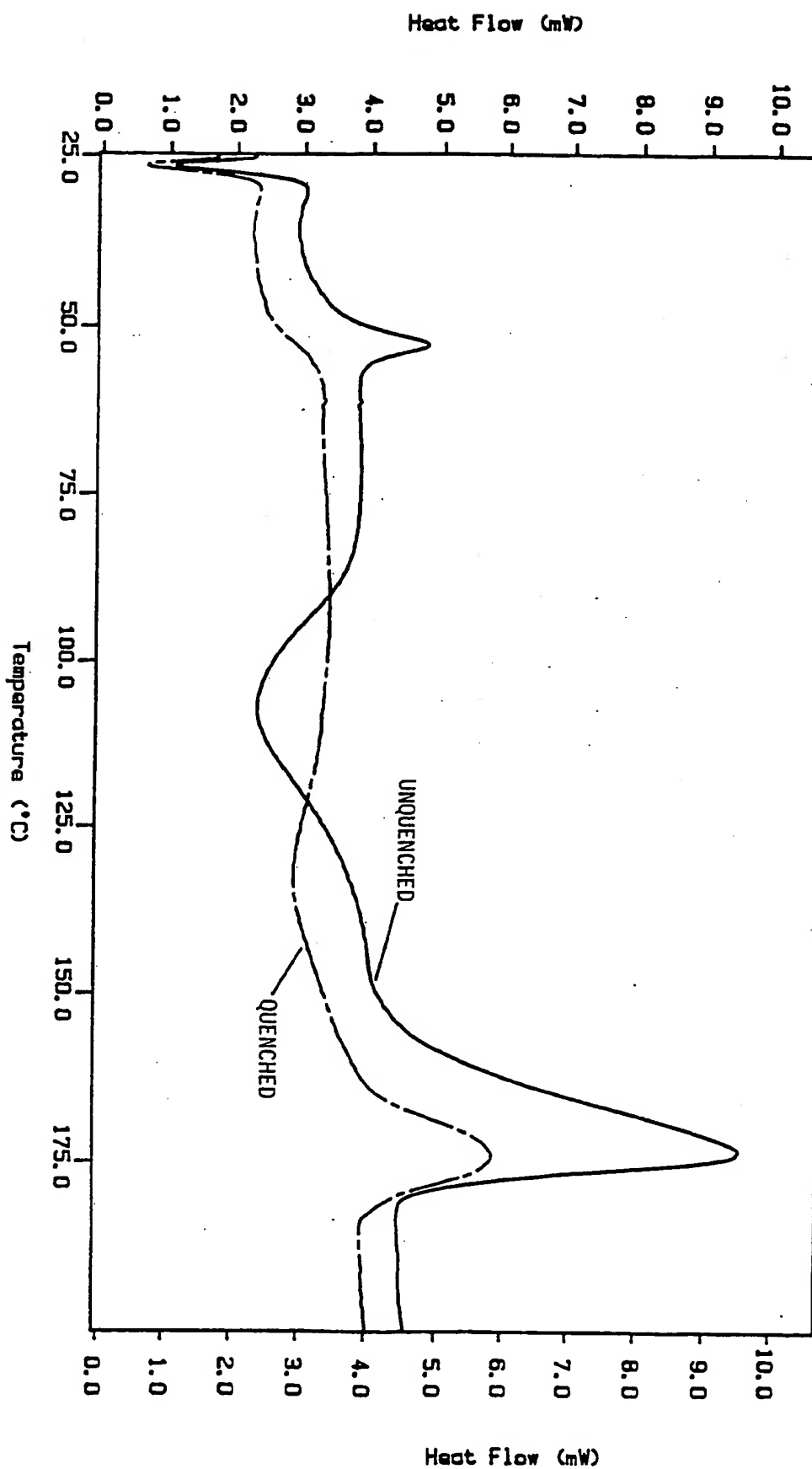


Figure 11. HOMOPOLYMER OF 100 PERCENT L-LACTIDE

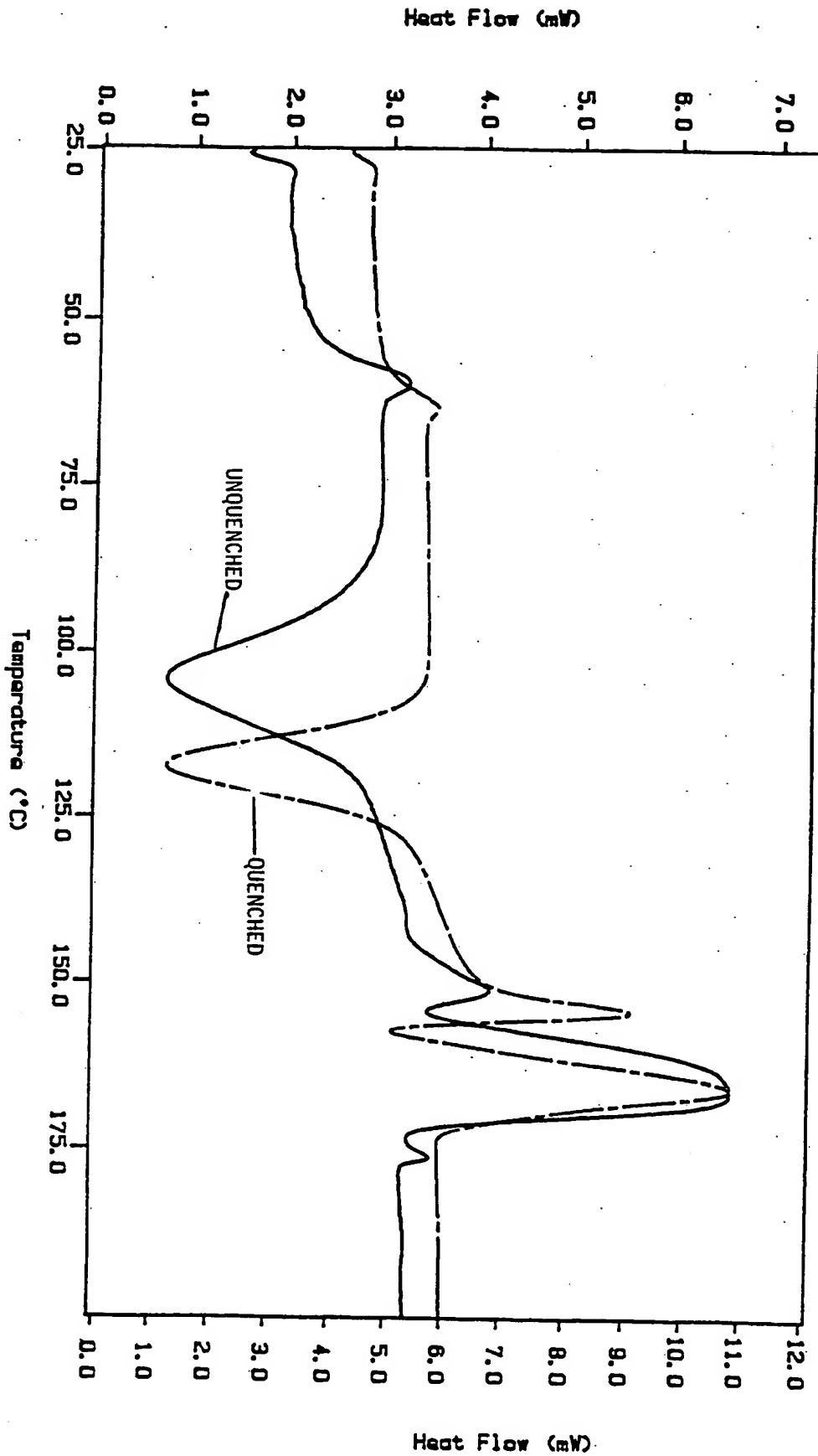


Figure 12. BLEND OF COPOLYMER AND HOMOPOLYMER

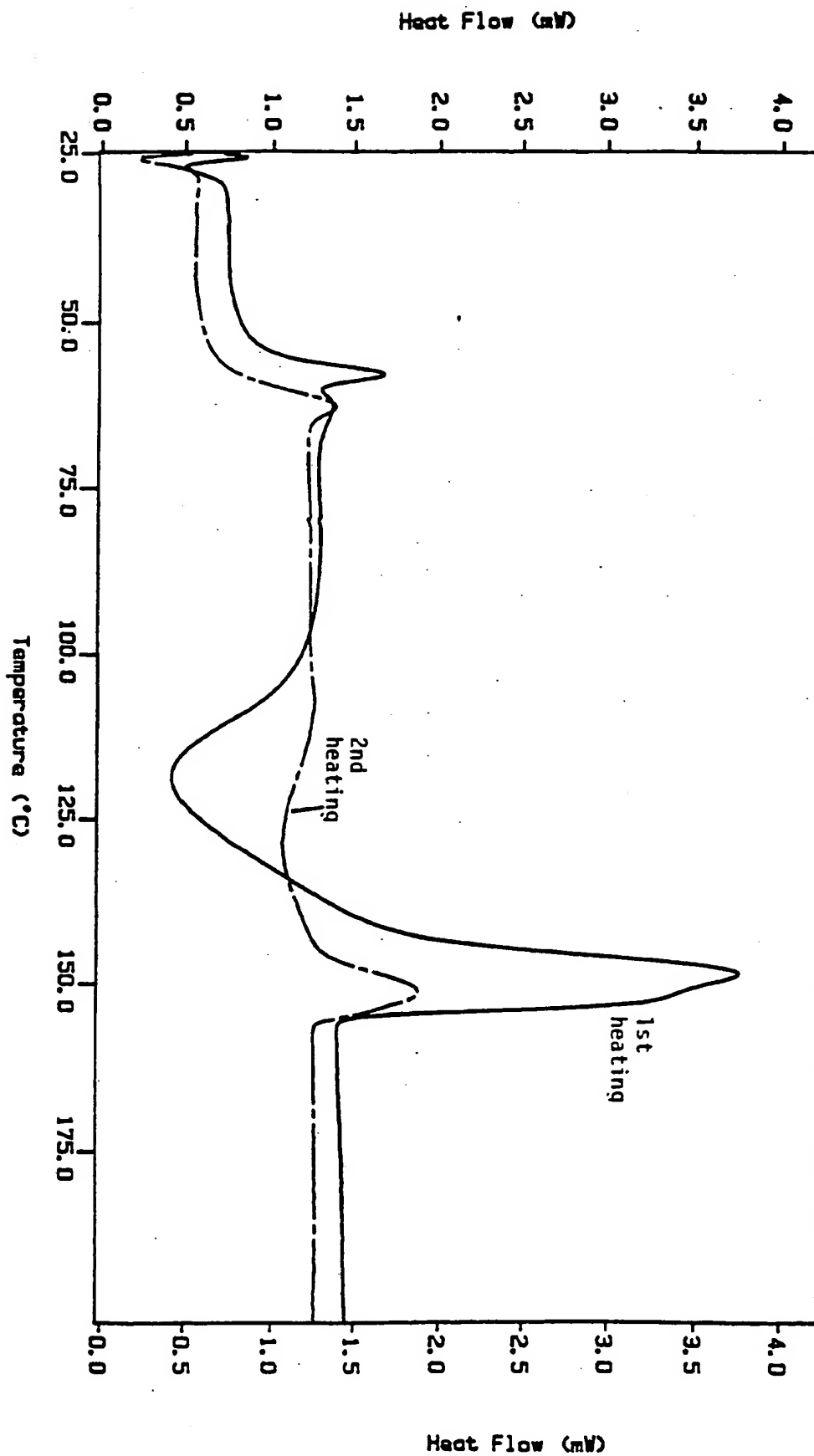


Figure 13. DSC OF 90/10, L-/D,L-LACTIDE COPOLYMER BLENDED WITH 5 PERCENT POLYSTYRENE

## INTERNATIONAL SEARCH REPORT

.. International Application No PCT/US 89/03380

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 L 67/04, C 08 G 63/08		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched †		
Classification System	Classification Symbols	
IPC5                      C 08 L; C 08 G		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ‡		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT*</b>		
Category †	Citation of Document, †† with Indication, where appropriate, of the relevant passages ‡‡	Relevant to Claim No. ‡‡
P,Y	Chemical Abstracts, volume 110, no. 24, 12 June 1989, (Columbus, Ohio, US), Bodmeier R. et al : "The effect of the addition of low-molecular weightpoly(DL-lactide) on drug release from biodegradable poly(DL-lactide) drug delivery systems. ", see page 409, abstract 219007f, & Int.J.Pharm. 1989, 51( 1), 1- 8	1-4,7
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Y	Chemical Abstracts, volume 108, no. 18, 2 May 1988, (Columbus, Ohio, US), Nakamura T. et al : "Surgical application of biodegradable films prepared from lactide--caprolactone copolymers. ", see page 391, abstract 156432b, & Adv. Biomater 1987, 7(), 759- 64	1-4,7
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<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: †‡</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 6th December 1989	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">12 JAN 1990</div>	
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorised Officer <div style="text-align: right; font-weight: bold; font-size: 1.2em;">T.K. WILLIS</div>	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Chemical Abstracts, volume 105, no. 19, 10 November 1986, (Columbus, Ohio, US), Chawla Attar S et al : "In-vivo degradation of poly(lactic acid) of different molecular weights. ", see page 371, abstract 158776d, & Biomater., Med.Devices, Artif.Organs 1986, 13(3), 153- 62	1-46
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A	US, A, 4677191 (TANAKA ET AL) 30 June 1987, see abstract	1-46
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A	US, A, 4728721 (YAMAMOTO ET AL) 1 March 1988, see column 2, line 31 - line 40; column 5, line 2 - line 6; abstract	1-46
	--	
A	US, A, 2703316 (ALLAN K. SCHNEIDER) 1 March 1955, see column 1, line 33 - line 45; column 2, line 10 - line 31; claims 1-7	1-46
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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
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SA 31002

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4677191	30/06/87	EP-A-B- 0171907	19/02/86
		EP-A-B- 0172636	26/02/86
		JP-A- 61028521	08/02/86
		US-A- 4683288	28/07/87
		DE-A- 3567470	16/02/89
		DE-A- 3567471	16/02/89
US-A- 4728721	01/03/88	EP-A- 0202065	20/11/86
		JP-A- 62054760	10/03/87
		US-A- 4849228	18/07/89
US-A- 2703316	01/03/55	NONE	

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